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16. ABSTRACT The report gives results of a 3-year program to assess the environmental impact of petroleum refining atmospheric emissions. Emissions from fugitive and process emission sources were sampled, and emission rates were determined. The sampling methodologies used for baggable sources (valves, flanges, pump and compressor seals, relief valves) and process stacks (fluid catalytic cracking units, sulfur recovery units, process heaters) are described in this volume. Also included are descriptions of the experimental design for the sampling program and the analytical techniques employed in the field sampling segment of the assessment study. This volume details gas chromatograph/mass spectrograph techniques used to identify and quantitate organic species present in refinery streams and vapor emissions.

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by

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1.0 INTRODUCTION

The petroleum refining industry represents a major potential source of hydrocarbon air emissions in the United States. Petroleum is a natural product containing complex organic substances, some of which are known to be toxic. There is little recent information on the subject of refinery hydrocarbon emissions and even less on the quantities and identities of potentially toxic emissions. Uncontrolled or fugitive emissions result from leaks which can occur in virtually any hydrocarbon service. These emissions require specialized technology for measurement.

In this program Radian has performed sampling and characterization of fugitive hydrocarbon emissions from several refineries. The methodology is described in subsequent sections of this appendix.

The first step in designating specific sources for sampling was the choice of refineries. A rigorous sampling plan would include most of the refineries known to be operating in the United States. Such a large sampling plan would be virtually unmanageable as well as being cost-prohibitive. Therefore, a number of representative refineries were selected for sampling. Refinery age, size, and geographical location were used as selection criteria.

Differences among refineries due to their different geographical locations are seen primarily in the types of hazardous materials they generate. Location influences the quality of the crude oil processed, and the nature and relative quantities of the products manufactured. The latter affects the severity of the operating conditions used in the process units as well as the types of units encountered. All of these considerations affect the by-products that result from processing the crude, and will influence the quantities and types of atmospheric emissions.

It was not believed that location would have a direct effect upon rates of hydrocarbon emissions. Knowledge of the specific chemical species involved is not necessary for classification of overall leak rates from fugitive sources. A possible secondary effect of location could include differences in local regulatory philosophies.

It was decided that the location effect on hazardous species would be investigated by sampling refineries in four different geographical regions. These are:

- East Coast,
- Gulf Coast,
- West Coast, and
- Middle United States (Midwest and Mid-Continent).

Refinery Age and Size

Two of the principal parameters used in the selection of refineries for sampling were age and size. These variables affect such things as maintenance and degree of repair, quality of equipment, and equipment design. Their use as independent variables may not be entirely valid. A closer examination of these factors is given in this section.

Age

There is no doubt that age affects the characteristics of refinery equipment and might ultimately influence fugitive emissions. There is some question, however, about the level at which age becomes a significant variable. Various ages were investigated at one of three levels of complexity: age of the entire refinery, ages of individual process units and ages of individual pieces of equipment.

Problems with this method exist in its application to sampling and the utility of the data generated. Determination of the ages of various equipment pieces was difficult at best. Turnaround and maintenance records for individual emissions sources in each unit sampled were not available for the most part.

Size

Refinery size can have an effect on such things as the number and type of products manufactured, the number and type of hazardous species formed, the types of units available for sampling, the amount of effort put in on maintenance programs, and the quality of equipment purchased. The most obvious break in these factors is between very small and large refineries. In order to use size as some indication of complexity, it was decided that a realistic cut point is 50,000 bbl/day. A range of refinery sizes above and below this size was sampled to prevent bias toward any individual size.

Because of the definition of size, size and refinery or process age become interdependent variables. There are not many new refineries significantly smaller than 50,000 bbl/day.

Also, it is difficult to find many new process units in refineries that small. Although the logical solution was to pick hardware age as the variable, implementation would be difficult if not impossible. Therefore, refinery age and size was broken into three categories:

- old/small,
- old/large, and
- new/large.

Large and small have been defined. Old means any refinery having its oldest operating unit more than 20 years old. New means having units no older than 20 years.

Process Units

The operating temperature and pressure were expected to have major effects upon fugitive emissions from a source. They are classified as choice parameters. Many combinations of temperature and pressure can be found in refineries. For the purposes of this program, four pressure/temperature classifications were employed:

- high pressure/high temperature,
- low pressure/high temperature,
- high pressure/low temperature, and
- low pressure/low temperature.

These terms are defined as follows:

- pressure -

  high > 150 psig
  low < 150 psig, and

- temperature -

  high > 100° C,
  low < 100° C.

A single unit usually did not have each size, type, and service defined for each piece of hardware. The pressure/temperature classification given to each unit reflected only the operating conditions in its major equipment area, such as a reactor. In some cases several units within a given category were sampled to fill all of the required variable categories. The choice of units was made on an individual refinery basis, with as much diversity among units sampled as the differences among refineries allowed. In this way, the effect of refinery process and type on the rates and nature of emissions was evaluated.

2.0 FUGITIVE EMISSIONS

The methods developed for detecting fugitive hydrocarbon emissions and measuring the emission rates are described in this section of the appendix. The procedures for selecting random sources for inspection and measurement are discussed.

2.1 Baggable Sources

Baggable sources have been defined as those sources that can be completely enclosed and sealed in a manner sufficient to prevent any loss of material to the atmosphere from inside the enclosure or "bag." These sources represent the majority of the potential sources selected for testing at each refinery. They include valves, flanges, pump seals, compressor seals, drains and relief devices.

2.1.1 Baggable Sources Selection

This section details the procedures by which individual fugitive sources were selected for sampling. Selection criteria are given for choosing the refineries visited and units sampled. The important variables affecting baggable and nonbaggable sources are presented and discussed.

In evaluating all the possible variables which could affect fugitive emissions from refineries, it was useful to categorize these variables into choice parameters and correlating parameters. A choice parameter is defined as a variable that is expected to directly affect fugitive emissions in such a way that it should be set up as a category in planning the number of samples taken. Establishing a good set of choice parameters insures a statistically accurate sample.

All other factors which were thought to affect the level of fugitive emissions were used as correlating parameters. Pertinent information on each source sampled was recorded during field testing.

Baggable Source Selection - Important Variables

Variables thought to affect the fugitive emissions from baggable sources were classified into choice and correlating parameters. The variables were further defined according to availability and usefulness. Availability was determined from the degree of difficulty expected when obtaining the necessary data in the field. Some information, such as pressure or temperature, is readily available. Other facts, such as age of valve packing, might be unavailable.

The final usefulness of a variable in the computation of the fugitive emissions from a refinery was also considered. Some important variables were not categorized for sampling because of their lack of ultimate usefulness. For example, using the age of some equipment as a parameter may not be very useful. Most refiners do not know the age of valve packing or flange gaskets, for example.

The variables chosen for each type of fitting consisted of the characteristics of the fluid within the fitting and the physical characteristics of the fitting itself. Choice parameters were defined as variables that might directly affect fugitive emissions and were used in selecting the source distribution. The choice parameters used for each fitting type are listed in Table A2-1 and discussed further below.

Valves

Valves are potentially the most significant source of fugitive emissions in the modern refinery because of their number. While individual leaks may be quite small, the cumulative amount can be very high. There are many factors such as valve construction, operating conditions, and fluid properties which may affect the magnitude of atmospheric emissions from any given valve.

A distinction is made between in-line and open-end valves. Most refinery valves are in closed piping systems. In this situation, leakage around the valve seat would not enter the atmosphere. The piping downstream of some valves is open to the atmosphere, however. Examples of these are sample and drain valves. Almost all sample and drain valves handle low-temperature material, most are gate valves, most are installed in pipes having diameters under four inches, and they are used in block service. No further variable breakdown is needed to describe these services.

More variables are required to characterize in-line valves. Atmospheric emissions can occur at three points in these valves:

- valve stem seals,
- valve bonnet seals, and
- valve end seals.

TABLE A2-1. RANGE OF CHOICE VARIABLES FOR SCREENED BAGGABLE SOURCES

Baggable Source	Choice Variable	Variable Ranges Found for Screened Sources
Valves	Pressure	-10 - 3,000 psig
	Temperature	-190 - 925°F
	Fluid State	Gas, Liquid, 2-phase
	Service	In-line, Open-ended
	Function	Block, Throttling, Control
	Size	0.5 - 36 inches
Flanges	Pressure	-14 - 3,000 psig
	Temperature	-30 - 950°F
	Fluid State	Gas, Liquid, 2-phase
	Service	Pipe, Exchanger, Vessel, Orifice
	Size	1 - 54 inches
Pump Seals	Pressure	0 - 3,090 psig
	Temperature	0 - 800°F
	Capacity	0 - 100,000 gpm
	Shaft Motion	Centrifugal, Reciprocating
	Seal Type	Mechanical Seal, packed seal
	Liquid RVP	Complete range
Compressor Seals	Pressure	0 - 3,000 psig
	Temperature	40 - 300°F
	Shaft Motion	Centrifugal, reciprocating
	Seal Type	Packed, labyrinth, mechanical
	Lubrication Method	Hydrocarbon lubricant
	Capacity	0.06 - 66.0 MMSCFD
Drains	Service	Active, Wash-up
Relief Valves	Pressure	0 - 1,350 psig
	Temperature	40 - 1,100°F
	Fluid	Gas, Liquid

The valve stem seal is the primary source, since it must seal against a moving stem. There are several varieties of bonnet seals, but most refinery valves have a flanged bonnet seal. These should leak less than stem seals since the seal assembly is stationary. Valve end seals are made where the valve is fastened to the adjacent piping. Most refinery valves have flanged ends. These were sampled as flanges, and therefore will be discussed in a later section.

The factors selected as choice parameters are basically the same as those used on other fittings, i.e., size, operating conditions (temperature, pressure), and fluid phase. These are easily determined before sampling. One further choice parameter was applied uniquely to valves, that being valve function. Each valve was classed as a block valve or a throttling valve. Throttling valves were normal hand valves or automatically operated control valves. This parameter reflects the effects of frequency of operation and type of stem movement.

Flanges

Flanges are the most common refinery example of the larger set of pipe and vessel joints, which also include threaded fittings and welds. Threaded fittings are limited to small diameter low-pressure service, and thus are not a significant portion of the refinery joint population. Welds are almost as common as flanges, but are much less prone to leakage. Welds are generally pressure-tested before being put into service, and repaired if necessary. Once in service, the weld is nearly as strong as the piping itself. A leak can result from corrosion or erosion of the weld, but such a leak will enlarge itself rapidly and become noticeable to unit personnel. Failure of a weld in this manner is very serious. It would usually require immediate attention, because when one weld fails, all others and the line itself become suspect. The safety hazard dictates corrective action more strongly than the pollution aspect. Therefore, no general program of weld testing was conducted.

The flanges tested were divided into 16 categories, depending on the interaction of three variables. These variables are:

- size,
- fluid state (gas/liquid), and
- operating conditions (pressure/temperature).

The size of the flange was expected to be directly related to the potential emissions because the effective seal length is a function of the size. A variety of flange diameters from two inches to four feet or more were tested to quantify the leak rate/flange size relationship.

The fluid state has an obvious effect on the tendency to leak. If a gap exists between the gasket and the flange faces, the properties of the fluid within and the operating conditions will determine the leak rate. The most obvious division of fluid properties is into liquid or gas. Some materials are transported under pressure as a liquid, but emerge from a leak as a gas at ambient conditions. By definition, the state inside the line was considered as the characteristic state.

The operating conditions considered when categorizing flanges were represented by the four pressure/temperature combinations described earlier:

- high pressure/high temperature,
- high pressure/low temperature,
- low pressure/high temperature, and
- low pressure/low temperature.

These four rough categories served as a choice parameter to insure a statistically valid distribution.

Flanges connecting end pieces to vessels and heat exchangers are generally larger than typical in-line flanges. A separate flange category was established for vessel/exchanger/air-cooler flanges. Within this category of special service flanges, the choice variables were pressure/temperature category and gas/liquid service.

Pump and Compressor Seals

Pumps and compressors contribute significantly to the overall fugitive emissions problems because of leakage around the shaft seals. Pumps and compressors in refinery service utilize two basic types of seals, packed and mechanical. However, the designs of pump and compressor seals differ because of the difference in the fluids they handle. Pumps and compressors will be individually discussed below.

Pumps

Choice variables for pumps are listed below:

- pressure/temperature,
- size (capacity),

- shaft direction/seal type, and
- Reid vapor pressure.

The four combinations of pressure and temperature (P/T) were used as described previously. These operating conditions affect many other areas such as seal type, method of lubrication, and cooling methods. Several pumps can be found for each P/T combination in almost every refinery.

Pump capacity is generally an indicator of shaft size. The latter is the more important variable, but the shaft sizes of every pump in a refinery may not be readily available. Pump capacity better meets the three choice criteria:

- significance,
- availability, and
- usefulness.

Shaft direction/seal type is very significant as a choice parameter. Information about pump types is both available and easily used. The L.A. County Study[6] found that differences in the relative numbers of seals in each category (mechanical > packed/centrifugal > packed reciprocating) were compensated for by the average leak rates (packed/reciprocating > packed/centrifugal > mechanical) so that each category contributed about equally to the total quantity of hydrocarbon emissions.

The final significant choice variable is fluid properties. Highly volatile hydrocarbons were found to contribute 70 percent of the fugitive pump emissions in L.A. County;[6]

therefore, it was decided to take fluid properties into account in this study. The Reid Vapor Pressure (RVP) designations used in that study were changed to < 1.5 lbs RVP, 1.5 - 10.5 lbs RVP, and > 10.5 lbs RVP. This prevents gasoline and jet fuel from being grouped into the same volatility category as the heavier products.

Compressors

Choice parameters for compressor seals include pressure, temperature, shaft motion, seal type, lubrication method and capacity. The method of lubricating packed seals is an important consideration. Packed seals without external liquid lubrication will allow leakage of light hydrocarbons. Lubricated seals will primarily leak heavy liquid hydrocarbons. Mechanical seals usually require a lubricating/sealing fluid.

The types of shaft seals used in centrifugal compressors could affect emissions because both types of packed seals are used in similar service, as are both types of mechanical seals.

Pressure-Relief Devices

Pressure, temperature, and fluid phase were selected as choice parameters for pressure-relief devices. Temperature and pressure of operation should affect the rate of emission from pressure-relief devices. Higher pressures and temperatures will provide greater driving forces for leakage. The same four pressure/temperature categories described previously were retained here with the exception of the LP/LT category.

Pressure-relief valves are generally used in liquid service; they open in proportion to the pressure applied to them. Safety valves are used in gas service and pop fully open when the set pressure is exceeded. Thus, the type of valve operation is included in fluid state variables.

Process Unit Drains

Process drains are found in every operating unit in a refinery. The nature of the emissions from the drains is dependent on the hydrocarbons handled by the unit. Drains can be classified as active and wash-up types. The nature of the hydrocarbons handled by the unit, and the drain type, form the principal choice criteria. Both active and wash-up drains can be found in most refinery processes. There are more active drains than wash-up, however. Therefore, sampling drains in a representative number of the process units chosen for testing allows both choice criteria to be met.

Site Specific Sampling Plan

Structured flexibility formed the tone of the sampling plan. The structure assured that all needed measurement and analysis requirements were efficiently covered. Flexibility was maintained within a procedural framework to apply what was learned toward subsequent sampling and analysis.

The sampling plan structure consisted of outlining detailed procedures before sampling began. This included:

- identification of process units to be sampled,

- identification of number and type of fittings within units,

- specifying choice and correlating variables, and

- developing forms for recording screening, sampling, variables, and analysis results.

Each site-specific sampling plan reflected modifications due to what had been learned at previous refineries.

Baggable Source Selection - Field Selection

This section of the report contains a description of the techniques used in the field to preselect baggable fugitive emissions sources.

The preselection methods given in this section were used at the first nine refineries studied during the program. The preselection methods used in the latter refineries are given on page 24 of the report.

The primary goals of the preselection process were to obtain:

- a statistically unbiased set of fittings, selected in a random manner, and

- a wide range of correlating parameters or process conditions for each set of selected fittings.

The initial steps of the selection process were carried out prior to the start of field sampling. These steps included the selection of refineries and individual process units to be sampled, and the development of a format for the selection of individual sources.

The selection of individual baggable sources was done using piping and instrumentation diagrams or porcess flow diagrams supplied by the refiner. The approximate number of sources selected at each refinery was:

Valves	250 - 300
Flanges	100 - 750
Pumps	100 - 125
Compressors	10 - 20
Drains	20 - 40
Relief Devices	20 - 40

Selecting fittings from the process flow diagrams gave two important benefits. First, this method eliminated any bias which might have resulted had these fittings been selected in the field. That is, fittings which could be determined to be leaking by observation were not selected preferentially over nonleaking fittings or vice versa. Second, a wide variation in process conditions was desired. Using basic knowledge of the process operation, it was possible to distribute the allotted fittings such that a wide range in the values of variables thought to affect the emissions rate was obtained.

The selection method used in the field is detailed below for each type of baggable fitting.

Valve Selection

The most difficult choice parameter to select was the valve size. In most cases, a complete range of valve sizes was not present in an individual process unit. However, since many of the same process units were chosen in several refineries, an exact distribution within each individual unit was not considered essential.

In general, all of the different hydrocarbon streams within the process unit were incorporated into the valve selection process. When there was more than one valve for each process stream (as was most always the case), valves were selected to give a variety of temperature/pressure combinations for each process stream.

The selection of valves within each process unit was based on a format of the type illustrated in Figure A2-1. In general, the number of valves allotted to each final grouping was based roughly on the proportion of valves in the process unit corresponding to that grouping. For example, a larger fraction of the valves would be assigned to the gas/vapor groups in a gas processing unit than in a lube oil processing unit.

Pumps

Approximately 100 - 125 pumps were selected at each refinery. These pumps were distributed in proportion to the total number of pumps in each of the inspected process units. The selection of individual pumps was based on obtaining a wide distribution in process stream type, temperature, and pressure, although the pump sizes and physical characteristics were also

	Organization of Choice Variables					Typical Number of Allotted Valves
Selected Process Unit	In Line Valves					
		Gas/Vapor Service				
			Control Valves			
				Size		
					< 4"	1
					4 - 8"	2
					> 8"	1
			Block Valves			
				Size		
					< 4"	2
					4 - 8"	4
					> 8"	2
		Liquid Service				
			Control Valves			
				Size		
					< 4"	3
					4 - 8"	3
					> 8"	3
			Block Valves			
				Size		
					< 4"	7
					4 - 8"	7
					> 8"	7
	Open Ended Valves				Drain Valves	1
					Sample Valves	1
						44

Figure A2-1. Typical Valve Selection Format

considered. In addition, many spare pumps, (that is, pumps that were not running) were also selected. These are usually under pressure and were found to be sources of emissions.

Compressors

The number of compressors in hydrocarbon service in a refinery is not large. Since compressors tend to leak at relatively high rates, all compressors in hydrocarbon service were selected. Compressors in hydrogen service were also selected since recycle hydrogen and other impure hydrogen streams contain hydrocarbons and other gases. Virtually all compressors in the selected refineries were screened.

Pressure Relief Devices

Pressure relief devices were selected from process flow diagrams and by visual selection in the field. Only those devices which vented to the atmosphere were selected.

The choice parameters for pressure relief devices included temperature, pressure, and fluid type, that is, gas or liquid service. The number of liquid service relief devices which vented to the atmosphere, however, was very low.

Flanges

Flanges were selected in a manner similar to valves according to the format given in Figure A2-2. Again, a distribution in process stream type, temperature, and pressure was obtained.

	Organization of Choice Variables			Typical Number of Allotted Flanges
Selected Process Unit	Gas/Vapor Service			
		Size		
			< 6"	2
			> 6"	3
	Liquid Service			
		Size		
			< 6"	5
			> 6"	5
	Special Service			
		Orifice Flanges		1
		Exchanger Flanges		1
		Vessel Flanges		1
				18

Figure A2-2. Typical Flange Selection Format

Many flanges listed in the data base were selected in this manner. In some refineries, additional flanges were selected to increase the size of the data base. These flanges included primarily those associated with selected valves.

Drains

Two types of drains were inspected during the program. These included active drains (those used to drain various process streams) and washup drains. Although the location of active drains was not usually indicated on the process flow diagrams, they were still selected prior to entering the unit. This was accomplished by selected drains associated with pumps, towers, vessels, and other processing equipment. The location of washup drains, however, could not be predicted and these drains were visually and randomly selected after entering the process unit.

Source Tagging

After the preselection process was completed, the fittings chosen for study were located and tagged for identification. Selections which proved to be nonexistent or physically inaccessible were reselected from the process flow diagrams. Each fitting was then screened with a portable hydrocarbon detector, as discussed in the following section, to determine if sampling was required.

Source Selection - Effect of Maintenance on Valves

At several refineries the effect on emissions of simple valve maintenance was studied. Maintenance studies on emissions from pump seals were planned, but none were done.

Difficulties were encountered in locating leaking pump seals in the proper leak rate categories. In addition some pumps that were found to be leaking could not be adequately isolated for seal replacement. In some cases, there were no spare pumps available to replace the leaking pump. In other cases, it was felt that the time required and the cost incurred for seal replacement was not justified by the size of the leak.

To evaluate control technologies for reducing fugitive emissions from valves and to develop parameters for "offset" analyses using valve maintenance programs, data on the effectiveness of various types of maintenance activities are needed. In the last four sampled refineries, efforts were directed toward this aspect of the program.

The maintenance on valves included:

- simple adjustment/tightening of the packing gland, and
- injection of grease into the packing area, if this is practiced by the refinery.

Additionally, some valves were monitored for extended time periods to determine:

- the effectiveness of valve maintenanace over an extended period of time,
- the increase in emission rates for unmaintained valves, and

- the frequency of routine maintenance required to maintain selected emission reductions.

The number of valves required to make the above evaluations can be limited through selective experimental design. The wide variation in leak rates between valves can be circumvented by using paired measurement schemes for maintenance evaluations. Only valves with particular selected leak rates were studied.

The factors that were considered in selecting valves for the maintenance study were:

- Process stream group (gas/vapor streams, light and two-phase streams, and heavy liquid streams).

- Valve type (block/gate, block/other, control/globe, control/other).

- Leak rate or screening value range (500 - 5000 ppm screening value, 5001 - 50,000 ppm screening value, and > 50,000 ppm screening value).

In addition, data were collected on all of the parameters normally included in the program.

A total of 28 valves were proposed for study at each refinery. The distribution of these valves is shown in Table A2-2.

TABLE A2-2. DISTRIBUTION OF VALVES SELECTED FOR MAINTENANCE STUDY IN EACH REFINERY

		Valve Selection Categories[2] by Screening Values			
Process Stream Group	Valve Type[1]	Low (500-5,000 ppm)	Medium (5001-50,000 ppm)	High (≥ 50,000 ppm)	Total X's
I Gas-Vapor Streams	BG	XO	XO ☐	XO	10
	BO	O	X	X	
	CG	X	X	X ☐	
	CO	O	X	X	
II Light Liquid & Gas-Liquid Streams	BG	XO	XO	XO ☐	10
	BO	O	X	X	
	CG	X ☐	X	X	
	CO	O	X ☐	X	
III Kerosine & Heavier Streams	BG	X	X	X	8
	BO	O	X	O	
	CG	X	X ☐	X	
	CO	O		O	
Total X's		6	12	10	28

[1] Valve Type:
BG = Gate valves in block (on/off) service.
BO = Types of valves, other than gate valves, in block service.
CG = Globe valves in control (throttling) service.
CO = Types of valves, other than globe valves, in control service.

[2] Valve Selection Criteria:
X = Valve should be maintained in this proces stream group and screening value category.
O = Alternate choice of valve process stream group and screening value category if all "X" selections cannot be found.
☐ = Valve in this stream group and screening value category should be selected for leak rate measurement, but no valve maintenance is to be performed.

The following procedure was used for determining the effects and efficiencies of the maintenance practices on various types of valves.

- The required valves were found by screening with portable hydrocarbon detectors.
- Complete variable information was recorded for each selected valve.
- Each valve was rescreened and sampled.
- Routine type maintenance was performed on the valve (tighten packing gland, add grease, etc.).
- The valve was then rescreened and sampled.
- Selected valves were rescreened for several days.

The screening and sampling procedures are described in following sections of the appendix. The maintenance that was performed was defined as "directed" or "undirected." Directed maintenance involves simultaneous maintenance and screening of the source with a hydrocarbon detector. Maintenance activities are continued until no further reduction in hydrocarbon concentration can be achieved. Undirected maintenance consisted of the normal maintenance procedures without any hydrocarbon concentration monitoring during the activity.

Whenever possible, each maintained source was rescreened several times during a period of one to two weeks immediately following the maintenance. The purpose of this activity was to get an indication of the short-term effectiveness of directed and undirected maintenance.

Arrangements were made at some refineries to obtain some data regarding the long-term effects of maintenance on the reduction of emissions. In these cases, refinery personnel agreed to monitor selected maintained valves at intervals of one week to one month for a period of six months.

As part of the experimental study, quality control procedures were implemented. These generally consisted of replicate and multiple source screening, replicate source sampling, accuracy testing of the sampling train, frequent calibration checks, and frequent analysis of standard gases in the laboratory.

2.1.2 Screening

In order to minimize the number of sources which were bagged, a preliminary screening was carried out to determine the need for sampling. Those sources which were found to have screening values above 200 ppm were selected for possible emissions sampling. When it was determined that the leaks were absent, sampling was not done. As the data base was expanded, the screening value limit of 200 ppmv was found to correspond to a leak rate in the order of 0.0001 pound per hour.

All the choice and correlating variables were recorded, however, for all sources that were screened. The values were recorded on formatted data sheets. Examples of these data sheets are shown in Figures A2-3 through A2-8.

New selection criteria were instituted during testing activities at the fifth refinery. The data base was developed to the point where leak rates of some sources could be estimated from the screening values. Thus, some of the sources with low screening values were not sampled. Instead, their leak rates were estimated from their screening values.

There are several techniques that have historically been used to screen potential sources in the baggable classification for leaks. These include visual observation of vapor leaks, visual observation of liquid leaks or buildup of residue, and spraying with soap solution. These methods are commonly used in refineries as a means of identifying those equipment items in need of maintenance, repair, or replacement. All these methods are qualitative, however.

Many, if not the majority, of potential baggable emission sources have skin temperatures above 100°C. Above this temperature, the technique of spraying soap solution is unusable, since it vaporizes on the hot source. Any bubbles created by leaking vapors are indistinguishable from those created by the vaporizing solution.

In Radian's experience in screening these sources, significant leakage has been measured where none of the visual methods indicated a leak. For this reason, a more accurate indicator of leak rate was required to adequately identify those selected sources that require bagging.

1. Radian ID# ☐ V A ☐ (1 2 3 4 5 6 7 8) **2. Unit** ____________________

3. Refinery ID# ____________________

VARIABLES:

4. Pressure, psig ☐ (9 10 11 12)

5. Temperature, °F ☐ (13 14 15 16)

6. Gas or liquid (G, L) ☐ (17)

7. Line size, in ____________ ☐ (18 19)

8. Block or control (B, C) ☐ (20)

9. Valve type [GA - gate; PL - plug; GB - globe; DI - diaphragm; BU - butterfly; SL - slide; AN - angle; RM - ram] ☐ (21 22)

10. Age, yrs ☐ (23 24)

11. Stem movement [I - in/out; R - rotation; C - combination] ☐ (25)

12. Manufacturer ☐ (26 27) ____________

13. Matls of const ☐ (28 29) ____________

14. In-line/Open-ended (I/O) ☐ (30)

15. Vibration [N - none; S - slight; M - moderate; H - heavy] ☐ (31)

16. Open/Closed (O/C) ☐ (32)

17. Flow/No-Flow (F/N) ☐ (33)

PROCESS FLUID DESCRIPTION:

18. Name ☐ (34 35 36 37 38 39 40 41 42 43) ____________________

SCREENING DATA:

19. Date ☐ (44 45 46 47 48 49)

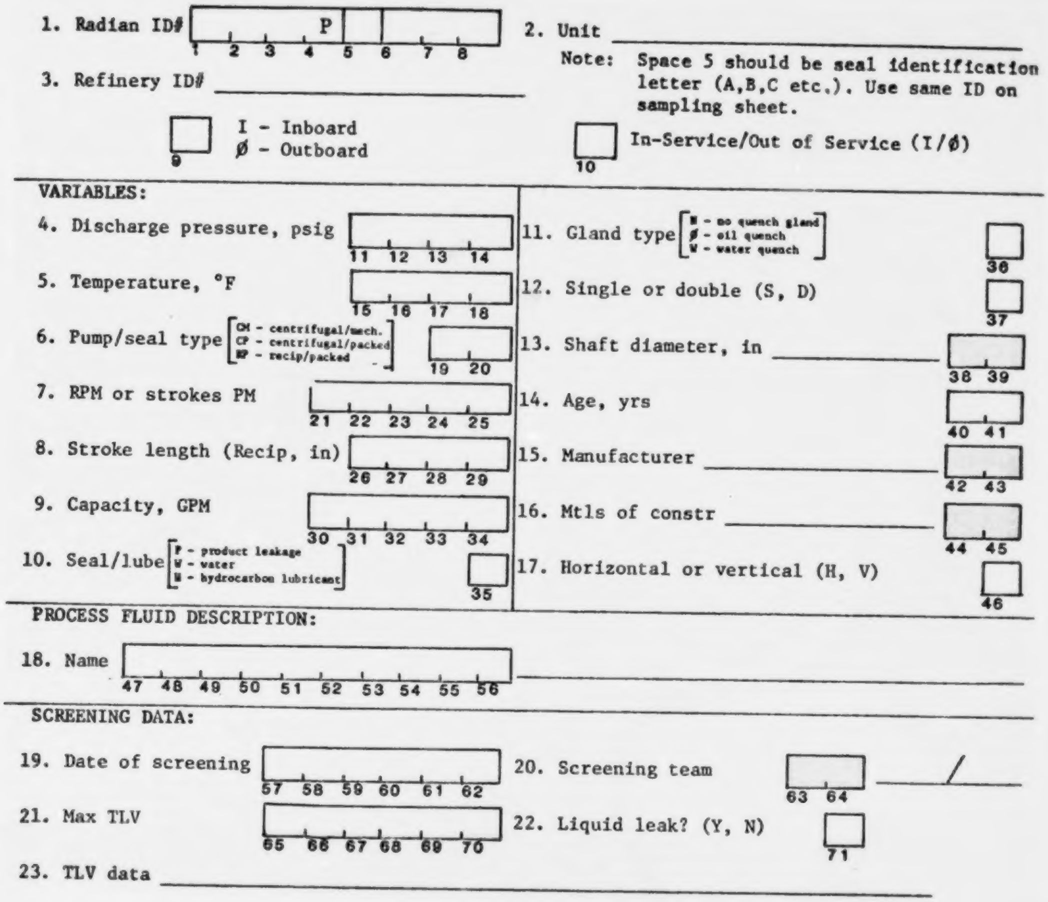
20. Screening Team ☐ (50 51) ______/______ **21. Stem TLV readings** ____________

22. Packing gland TLV ____________ **23. Stem & gland, max TLV** ☐ (52 53 54 55 56 57)

24. Liquid leak? (Y, N) ☐ (58)

Remarks:

Figure A2-3. Data Sheet - Valves



1. Radian ID# P
1 2 3 4 5 6 7 8

2. Unit ______

Note: Space 5 should be seal identification letter (A,B,C etc.). Use same ID on sampling sheet.

3. Refinery ID# ______

☐ 9 I - Inboard
Ø - Outboard

☐ 10 In-Service/Out of Service (I/Ø)

VARIABLES:

4. Discharge pressure, psig 11 12 13 14

5. Temperature, °F 15 16 17 18

6. Pump/seal type [CM - centrifugal/mech. CP - centrifugal/packed RP - recip/packed] 19 20

7. RPM or strokes PM 21 22 23 24 25

8. Stroke length (Recip, in) 26 27 28 29

9. Capacity, GPM 30 31 32 33 34

10. Seal/lube [P - product leakage W - water H - hydrocarbon lubricant] ☐ 35

11. Gland type [N - no quench gland Ø - oil quench W - water quench] ☐ 36

12. Single or double (S, D) ☐ 37

13. Shaft diameter, in ______ 38 39

14. Age, yrs 40 41

15. Manufacturer ______ 42 43

16. Mtls of constr ______ 44 45

17. Horizontal or vertical (H, V) ☐ 46

PROCESS FLUID DESCRIPTION:

18. Name 47 48 49 50 51 52 53 54 55 56 ______

SCREENING DATA:

19. Date of screening 57 58 59 60 61 62

20. Screening team 63 64 ___/___

21. Max TLV 65 66 67 68 69 70

22. Liquid leak? (Y, N) ☐ 71

23. TLV data ______

Remarks:

Figure A2-4. Data Sheet - Pump Seal

1. **Radian ID#** ☐ C 0 (1 2 3 4 5 6 7 8) 2. **Unit** ____________________

3. **Refinery ID** ____________________

VARIABLES:

4. **Discharge pressure, psig** ☐ (9 10 11 12)

5. **Temperature, °F** ☐ (13 14 15 16)

6. **Comp/seal type** ☐ (17 18)
   - R/P - recip/packed
   - R/L - rotating/labyrinth
   - R/R - rotating/rest. ring
   - R/M - rotating/mech.
   - R/Q - rotating/liquid

7. **RPM or strokes PM** ☐ (19 20 21 22 23)

8. **Stroke length (Recip, in.)** ☐ (24 25 26 27)

9. **Capacity, MMSCFD** ☐ (28 29 30 31 32)

10. **Seal/lube** ☐ (33)
    - P - product leakage
    - W - water
    - H - hydrocarbon lubricant

11. **Gland type** ☐ (34)
    - N - no quench gland
    - 0 - oil quench
    - W - water quench

12. **Single or double (S, D)** ☐ (35)

13. **Shaft diameter, in** ____________ ☐ (36 37)

14. **Age, yrs** ☐ (38 39)

15. **Manufacturer** ____________ ☐ (40 41)

16. **Mtls of constr** ____________ ☐ (42 43)

17. **Cylinder loading, %** ☐ (44 45 46)

18. **In-Service/Out-of-Service (I/0)** ☐ (47)

PROCESS FLUID DESCRIPTION:

18. **Name** ☐ (48 49 50 51 52 53 54 55 56 57)

Brief description ____________________

____

SCREENING DATA:

19. **Date of screening** ☐ (58 59 60 61 62 63) 20. **Screening team** ☐ (64 65) ____________

21. **Max TLV** ☐ (66 67 68 69 70 71) 22. **Liquid leak? (Y, N)** ☐ (72)

23. **TLV readings** ____________________

Remarks:

Figure A2-5. Data Sheet - Compressor Seal

1. Radian ID# ☐☐☐☐R☐V☐☐☐ 1 2 3 4 5 6 7 8   2. Unit ______________________

3. Refinery ID# ________________________

VARIABLES:

4. Pressure, psig ☐☐☐☐ 9 10 11 12

5. Temperature, °F ☐☐☐☐ 13 14 15 16

6. Gas or liquid (G, L) ☐ 17

7. Line size, in ____________ ☐☐ 18 19

8. Single or double (S, D) ☐ 20

9. Vented [A - to atmosphere
B - to combined header to flare] ☐ 21

PROCESS DESCRIPTION:

10. Name ☐☐☐☐☐☐☐☐☐☐ 22 23 24 25 26 27 28 29 30 31 ________________________

SCREENING DATA (Only for atmospheric-vented valves):

11. Date of screening ☐☐☐☐☐☐ 32 33 34 35 36 37   12. Screening team ☐☐ 38 39 __________

13. TLV readings ____

14. Max TLV ☐☐☐☐☐☐ 40 41 42 43 44 45   15. Liquid leak? (Y, N) ☐ 46

Remarks:

Figure A2-6. Data Sheet - Relief Valve

1. Radian ID# ☐☐☐☐☐☐☐☐ 1 2 3 4 5 6 7 8   **2. Unit** ____________________

3. Refinery ID# ______________________

VARIABLES:

4. Pressure, psig ☐☐☐☐ 9 10 11 12

5. Temperature, °F ☐☐☐☐ 13 14 15 16

6. Gas or liquid (G, L) ☐ 17

7. Line size, in __________ ☐☐ 18 19

8. Type ☐☐ 20 21
- WE - weld
- TH - threaded
- FF - flat face
- RF - raised face
- FH - floating head tube sheet

9. Special service ☐ 22
- A - air cooler
- O - orifice plate
- V - vessel/exch.

10. Age, yrs ☐☐ 23 24

11. Mts. of const. __________ ☐☐ 25 26
- ST - steel
- OT - other

12. Manufacturer __________ ☐☐ 27 28

13. Gasket mtl __________ ☐☐ 29 30

14. Vibration ☐ 31
- N - none
- S - slight
- M - moderate
- H - heavy

PROCESS FLUID DESCRIPTION:

15. Name ☐☐☐☐☐☐☐☐☐☐ 32 33 34 35 36 37 38 39 40 41 ____________________

SCREENING DATA:

16. Date of screening ☐☐☐☐☐☐ 42 43 44 45 46 47   **17. Screening team** ☐☐ 48 49 ______/______

18. Liquid leak (Y, N) ☐ 50

19. TLV readings ______________________________

20. Max TLV ☐☐☐☐☐☐ 51 52 53 54 55 56

Remarks:

Figure A2-7. Data Sheet - Flange or Weld

1. Radian ID# | | | | D | R | | | |
1 2 3 4 5 6 7 8

2. Unit ______________________ 3. Refinery ID#______________

VARIABLES:

4. Active or wash-up? (A, N) ☐
9

5. Visible vapor emission? (Y, N) ☐
10

6. Temperature of input, °F | | | | |
11 12 13 14

7. Rectangular or circular opening? (R, C) ☐
15

8. Diameter if circular (in.) | | | | |
16 17 18 19

9. Length if rectangular (in.) | | | | |
20 21 22 23

10. Width if rectangular (in.) | | | | |
24 25 26 27

DESCRIPTION OF INPUT TO DRAIN:

11. Name | | | | | | | | | | | ______________________
28 29 30 31 32 33 34 35 36 37

SCREENING DATA:

12. Date of screening | | | | | | |
38 39 40 41 42 43

13. Screening team | | | ______________________
44 45

14. Max TLV | | | | | | |
46 47 48 49 50 51

15. TLV readings ______________________

Remarks:

Figure A2-8. Data Sheet - Unit Drain

Instrumentation

A Bacharach Instrument Company J-W Model TLV Sniffer has been found to be useful for the screening of baggable sources. This instrument utilizes a catalytic combustion detector to measure low concentrations of flammable vapors. It can detect hydrocarbon concentrations as low as 1.0 ppm. Three concentration scales, 0 - 100 ppm, 0 - 1,000 ppm, and 0 - 10,000 ppm, are built into this instrument. A dilution probe was used when the TLV readings exceeded 10,000 ppm which allowed readings of up to 100,000 ppm. The instrument meter displays the result as ppm hexane by volume when calibrated with hexane. It is battery operated, self-contained, compact and portable. The instrument performance has been very satisfactory.

A second instrument used to screen for hydrocarbon emissions was the Century Instrument Company Organic Vapor Analyzer (Model OVA-108). This instrument utilized a flame ionization detector to measure hydrocarbon concentrations. The role of the OVA was limited to obtaining original screening values only. When leaking sources were identified, they were rescreened with the TLV Sniffer when the source was sampled.

Recommended Calibration Procedure for the TLV Sniffer

Each of the concentration ranges on the TLV Sniffer must be calibrated separately. This requires different hexane-air standards. The recommended concentrations for each of these standards are given below:

TABLE A2-3. TLV CALIBRATION STANDARDS

Concentration Range on TLV	Recommended Calibration Standard Concentration; ppmv hexane in air
0 - 100 ppmv range (x 1)	None[a]
0 - 1,000 ppmv range (x 10)	200-900 ppmv hexane
0 - 10,000 ppmv range (x 100)	2,000-5,000 ppmv hexane

[a] It was not felt necessary to calibrate this low range since 200 ppm was the cut-off point for sampling.

Teflon or Tedlar sample bags were used during the calibration procedure. Each bag was labeled with the concentration of the assigned standard gas. The bags were not filled with any gas, other than the assigned standard.

The step-by-step procedure for calibrating the TLV is given below. The calibration was done at the beginning of each day the TLV was used.

(1) Clean the sample probe and hose with methylene chloride. Dirt or other accumulation in these areas can have a pronounced effect on the concentration reading, particularly in the dilution probe mode. Residual methylene chloride can be removed more quickly by blowing air through the probe and hose.

(2) Turn on the TLV and check the battery charge level. Allow 10 minutes warm-up time before starting the calibration.

(3) Remove the plastic casing from the TLV and locate the three small adjustment screws. These are labeled x1, x10, and x100, corresponding to the concentration ranges indicated on the mode selector switch.

(4) Place the instrument in an upright position. Changing the position of the instrument will affect the distribution of heat in the catalytic element and change the meter reading.

Each of the concentration scales must be calibrated independently. Hence, the following steps (5 through 9) should be performed for one of the concentration scales and then repeated for each of the others. Also, make sure that the dilution air intake holes in the dilution probe are completely covered by the black rubber ring during the entire calibration procedure.

(5) Flush the calibration bag by filling it with the appropriate gas standard. Then, compress the bag to remove as much gas as possible. Repeat this procedure twice.

(6) Fill the sample bag with calibration gas.

(7) Attach a small length of rubber tubing to one of the valves on the bag. Manually pinch off the tubing and open the valve by spinning the bag. Place the end of the rubber tubing over the TLV probe and allow the standard gas to enter the TLV for about

10 seconds. Pinch off the rubber tubing and remove the rubber tube from the probe.

(8) While keeping the tube clamped, wait till the meter reading has stabilized. Zero the meter on the appropriate scale using the fine and/or coarse adjustment controls.

(9) After zeroing the meter, allow more standard gas to enter the TLV. The bag should hang freely from the end of the probe, i.e., no external pressure should be applied on the bag. Turn the appropriate adjustment screw until the meter reading corresponds to the concentration of the standard gas. If a substantial adjustment is required, it will be necessary to rezero the meter and repeat the calibration (steps 8 and 9).

The probe can also function as a dilution probe. This extends the range of the TLV from 10,000 ppm to 100,000 ppm. To operate the dilution probe, the black rubber washer is pulled back to expose the dilution air intake holes. In this mode, the meter will read a concentration which is approximately one-tenth of the actual concentration.

This dilution factor can be verified by reading the high-range (x100) gas standard with the meter zeroed on the mid-range (x10) scale. The dilution factor is calculated as follows:

$$\text{Dilution factor} = \frac{\text{ppmv, calibration gas}}{\text{ppmv, meter reading}} \cong 10$$

All subsequent screening results are multiplied by the dilution factor obtained here.

Preparation for Screening

The following equipment was included in the field screening gear:

- Recording equipment, notebook, data sheets, pens, etc.

- TLV Sniffer, hose, and dilution probe.

- Extra cotton filters, pipe cleaners, and paper towels.

- Knapsack or similar for carrying equipment to elevated sources.

In order to insure that all screening results are obtained on an equivalent basis, the following procedures are recommended.

- The battery pack should be fully recharged before the start of screening. Generally, an overnight charge is sufficient to provide eight hours of continuous screening time.

- The TLV Sniffer and the dilution probe should be calibrated before the start of each sampling day.

- Ten minutes warm-up should be allowed before screening.

- The meter (xl scale) should be zeroed before screening each source. The meter can be zeroed in any open area since ambient hydrocarbon readings are usually quite low.

- The small orifice in the dilution probe should be free of dirt or other accumulation. When a source is encountered which requires the use of the probe in the dilution mode, the dilution orifice should be inspected. In addition, the small diameter extension and the cotton filter chamber sections of the probe should be inspected and cleaned frequently. If the cotton filter gets wet, it should be replaced.

- Screening should always be done with the meter in an upright position, as the meter position affects the distribution of heat in the catalytic element.

Common Operating Problems

There are several situations which may arise that could cause difficulties in obtaining proper results. Some of the more common problems are discussed below.

On some TLV Sniffers, the zeros for each of the three concentration ranges may not coincide. If this is the case the magnitude of the difference should be determined and screening values adjusted accordingly. For example, assume that the meter has been zeroed on the (xl) scale and a reading of 500 ppm is obtained when the meter is switched to the (x100) scale. In this case, 500 should be subtracted from all readings taken on the (x100) scale. Small differences from one scale to the next, however, may be neglected.

In some cases, it may be difficult to determine whether a meter response is due to high ambient air hydrocarbons or a source leak, particularly when the ambient reading is highly variable. This problem is commonly experienced in compressor houses or other enclosed areas. One method to determine if the source is leaking is to place the probe at the leak source and then remove it from the leak source. This operation is repeated at regular intervals. If the movement of the needle corresponds to the placement and removal of the probe (keeping in mind the two-second time lag), the source is probably leaking. The screening value is then determined by subtracting the ambient reading from the measured screening result. A variety of such situations may be encountered and a judgment on the part of the operator may be required to obtain a representative reading.

Occasionally, a source may be encountered which has a highly variable leak rate. The design of the TLV Sniffer tends to damp these variations somewhat; however, some oscillation in the reading may still occur. In general, the maximum sustained reading or the maximum repeatable reading should be recorded. Again, a judgment on the part of the operator may be required to obtain a representative reading.

One further screening difficulty may arise when screening sources which contain heavier hydrocarbon streams, particularly on hot sources. When these valves are screened some of the vapor tends to condense on the internal probe-sample hose surfaces. The response of the meter is considerably slower for these sources relative to that seen when screening lighter hydrocarbons. And, the meter may require more time to return to zero. When screening this type of source, the meter should be allowed to stabilize before recording the result. The meter should be allowed to return to about 20 percent of the recorded value before moving to the next screening point. Prior to screening the next source, sufficient time should be allowed for the meter to stabilize or return to zero. Often the meter will not return completely to zero and a considerable adjustment may be required.

Under no circumstances should the end of the probe be placed in contact with liquid. If liquid is drawn through the sample hose, it will damage the catalytic element. A liquid trap, connected between the TLV Sniffer and the sample hose, was used. This gave some protection against damage to the element.

Screening Procedures

The procedure used for screening with the TLV Sniffer was quite simple. The sample probe was held as close as possible to the suspected leak source. This reduced the effect of the wind and increased the reproducibility of the readings. The screening procedure differed slightly for each baggable source type as discussed below.

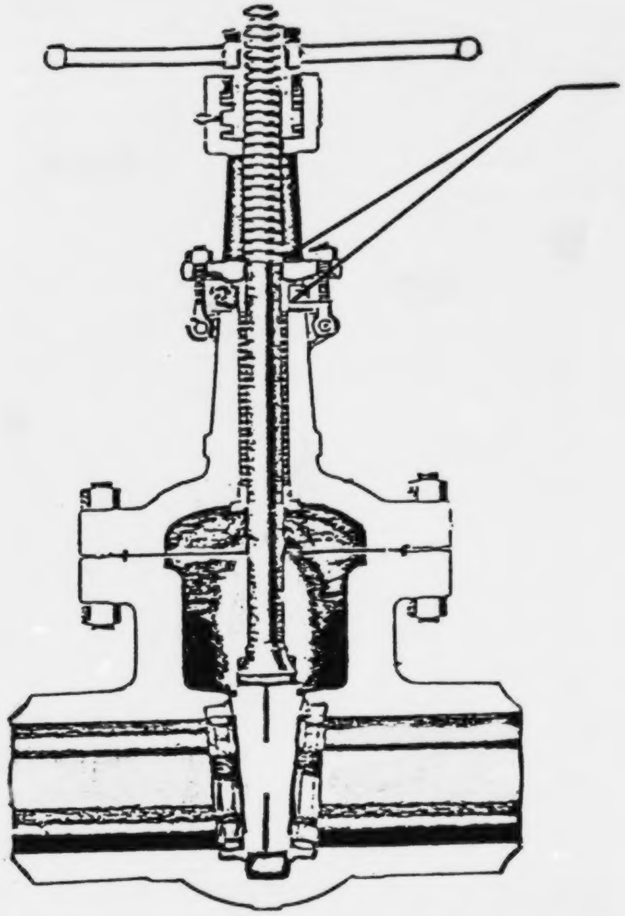
Valves Screening Methods

Most of the valves that were selected for screening were either gate, globe, or control valves. Hydrocarbon leaks from these valves occur at the stem and/or the packing gland, as indicated in Figure A2-9. Some plug valves were also selected. Hydrocarbon leaks from this type of valve can occur at the plug square or under the malleable gland, as indicated in Figure A2-10.

Both the stem and the packing gland of selected valves were screened. The probe locations used included the four arbitrary compass points around the seal, relative to the valve casing. Thus, a total of eight such readings were taken for each valve. In addition, two more readings (one for the stem and one for the glands) were obtained at a distance of 5 cm (using a wire extension as a guide) from the leak source. The probe was rotated in a circular path around the leak source and the maximum reading was recorded.

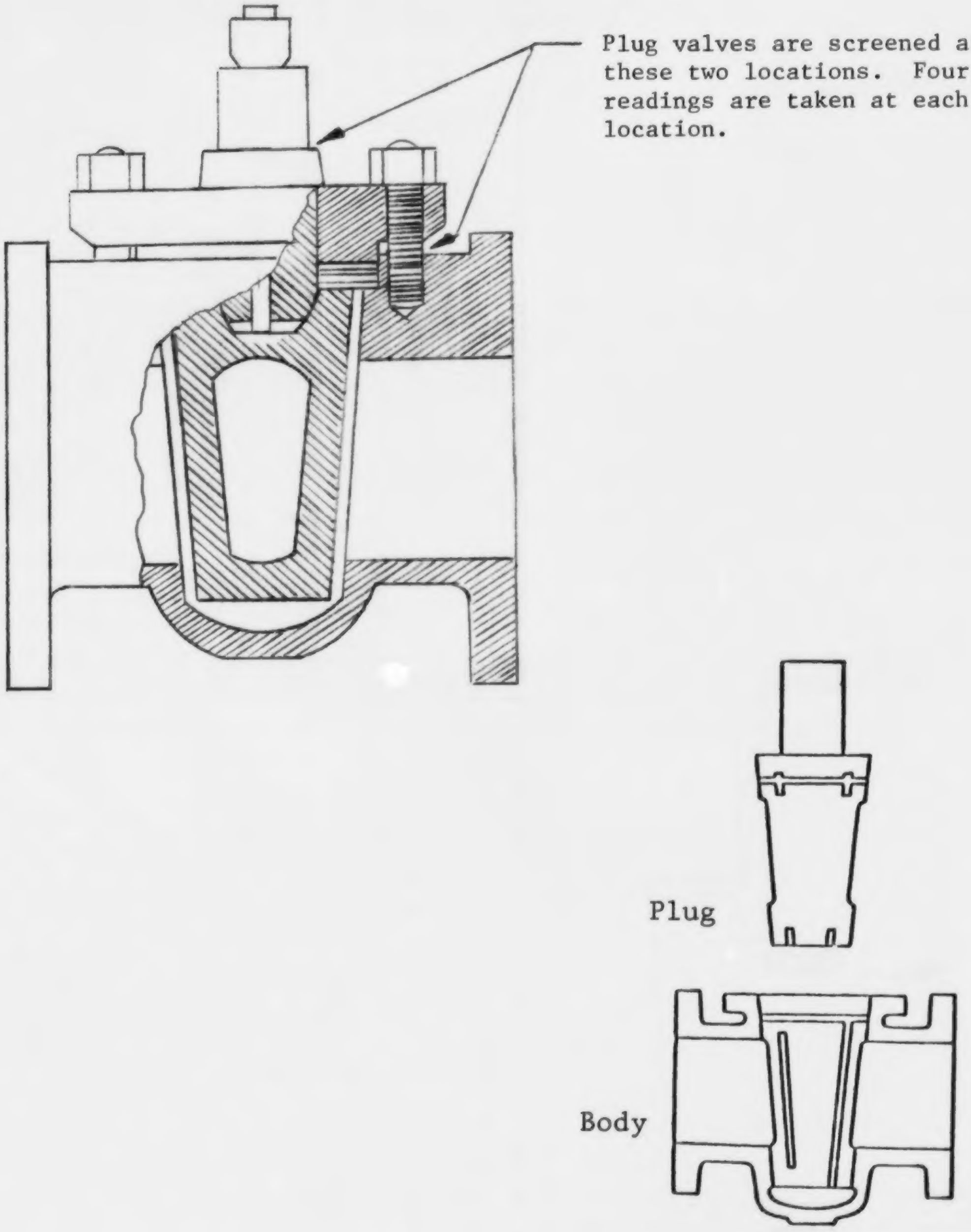
Flanges

Flanges were screened by placing the TLV Sniffer probe at two-inch intervals around the perimeter of the flange.



Gate, globe, and
control valves are
screened at these
two locations. Four
readings are taken at
each location.

Figure A2-9. Gate Valves



Plug valves are screened at these two locations. Four readings are taken at each location.

Figure A2-10. Plug Valves

After locating the maximum leak point, three additional readings were taken at the remaining compass points, relative to the location of the maximum leak point. All four readings were recorded.

Pump and Compressor Seals

Pump seals were screened in a manner similar to that used for screening valves. Leakage occurs around the rotating shaft at the point where it enters the pump housing. The Bacharach TLV Sniffer probe was placed as close as possible to the potential leak point around the shaft at the pump housing. Prior to this, the instrument was zeroed at ambient conditions. Four readings were taken at points 90 degrees apart around the shaft. Also, the maximum readings, taken at a distance of 5 cm, were recorded. The probe was left at each point for a minimum of 5 seconds. The detection of hydrocarbon at a concentration of 200 ppm at any of the four points resulted in the pump being bagged and sampled.

Large pumps or pumps in severe services may have two seals, an inboard seal and an outboard seal. In these cases, each seal was screened separately.

The screening procedure for compressors depended on the accessibility of the seal area. If the seal area was accessible, the screening procedure was identical to that for pumps. After zeroing at ambient conditions, the TLV Sniffer probe was placed at four locations 90 degrees apart around the shaft and right at the point where the shaft enters the compressor housing. A hydrocarbon concentration of 200 ppm or more at any point indicated the need for bagging and sampling of the seal.

In many cases the seal area was enclosed and hydrocarbons leaking from the seal were vented to the atmosphere or to a vapor recovery system. When compressors vented to the atmosphere were encountered, they were screened and sampled, if necessary, at the point where the vent pipe discharged to the air. The TLV probe was positioned at a point located just inside the end of the vent.

Compressors often have more than one seal. Each seal was individually screened and, if necessary, bagged and sampled.

Pressure-Relief Devices

Only those pressure-relief devices that are vented to the atmosphere were screened. Those devices that are vented to blowdown and flare systems can only leak to the atmosphere at the connecting flanges, and these leak sources are considered to be flanges.

The relief valves were screened using the Bacharach TLV Sniffer. After zeroing the instrument at ambient conditions, the probe was placed at two-inch intervals around the perimeter of the vent (horn) just at the exit. The probe was also placed at the center of the vent opening at a level with the vent exit.

When the top of the horn was inaccessible, a screening value was obtained at the weep hole, located near the bottom of the horn. The probe was left at each location for a minimum of five seconds. If a hydrocarbon concentration of 20 ppm was detected during this five-second period, the probe was left in place for at least an additional five seconds. The maximum TLV readings during the ten-second period were recorded.

If any readings exceeded 200 ppm, the relief device was to be sampled and bagged.

Drains

In this program, process unit drains were classified as either active or washup drains. The screening process is the same for both types.

The Bacharach TLV Sniffer was zeroed at ambient conditions. Then the probe was placed at two-inch intervals around the perimeter of the drain. At each of these points, the probe was placed right at the inside edge of the drain at the level of the exit. The probe was left in place for at least five seconds. If, during this time period, a hydrocarbon concentration in excess of 20 ppm is detected, the probe was left in place for an additional five seconds. The maximum concentration detected in this ten-second period was recorded.

Upon completing the traverse around the perimeter of the drain, one additional reading was taken at the center of the drain. The maximum of the perimeter and center readings was recorded and used as the basis for sampling decisions. If the maximum individual value was equal to 200 ppm hydrocarbon or greater the drain was bagged and sampled.

2.1.3 Sampling Train

The method preferred for sampling leaks from baggable sources is the dilution or flow-through method. The sampling trains that were used in this method are shown in Figures A2-11 and A2-12. The train was contained on a portable cart, which could be easily pushed around the unit from source to source.

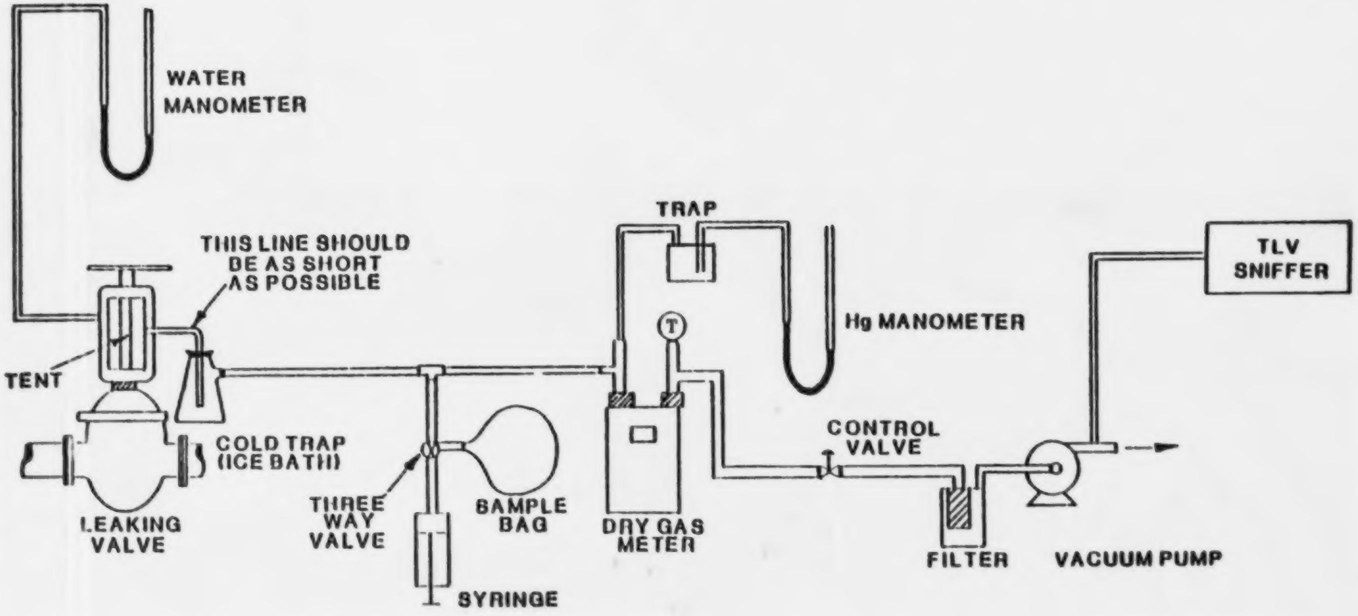

WATER
MANOMETER
THIS LINE SHOULD BE AS SHORT AS POSSIBLE
TENT
COLD TRAP (ICE BATH)
LEAKING VALVE
THREE WAY VALVE
SYRINGE
SAMPLE BAG
TRAP
T
DRY GAS METER
Hg MANOMETER
CONTROL VALVE
FILTER
VACUUM PUMP
TLV SNIFFER

Figure A2-11. Sampling Train for Baggable Sources of Hydrocarbon Emissions: Flow-Through Method Using a Syringe

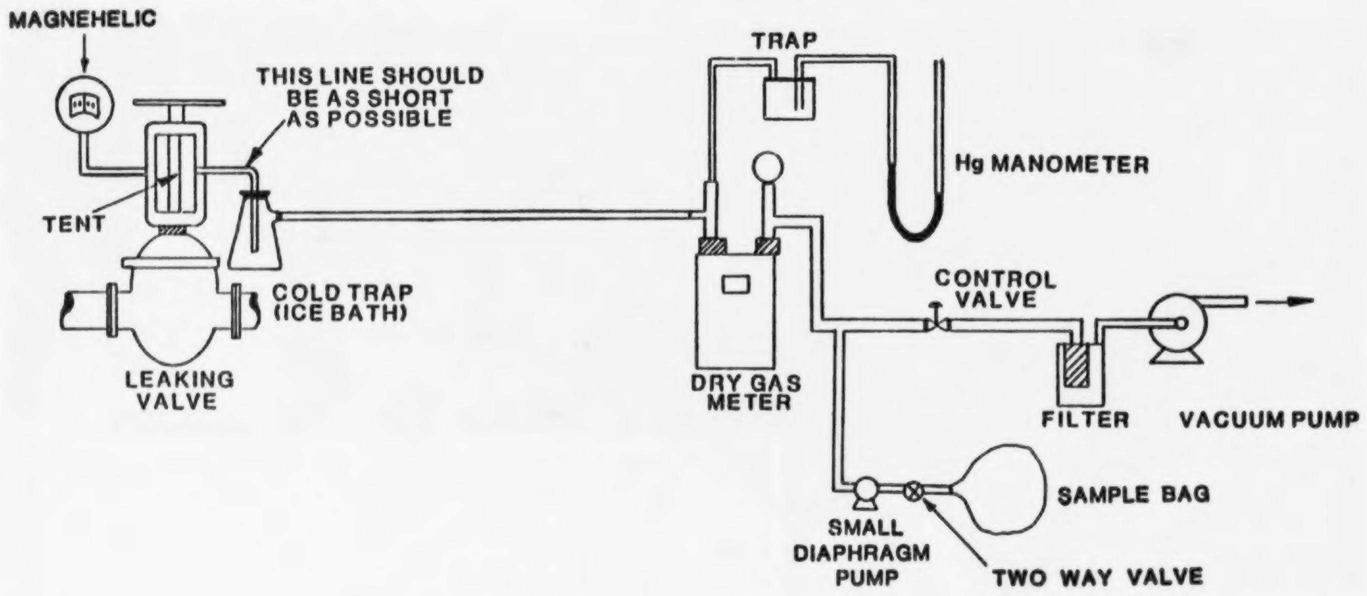

MAGNEHELIC
THIS LINE SHOULD BE AS SHORT AS POSSIBLE
TENT
COLD TRAP (ICE BATH)
LEAKING VALVE
TRAP
Hg MANOMETER
DRY GAS METER
CONTROL VALVE
FILTER
VACUUM PUMP
SAMPLE BAG
SMALL DIAPHRAGM PUMP
TWO WAY VALVE

Figure A2-12. Sampling Train for Baggable Source of Hydrocarbon Emissions Using a Diaphragm Sampling Pump

The major equipment items in the sampling train were the vacuum pump used to draw air through the system, and the dry gas meter used to measure the flow rate of gas through the train.

The vacuum pump as a 4.8 CFM Teflon-ring piston-type equipped with a 3/4 horsepower air-driven motor. Low pressure air (~ 100 psig) is available at or near most refinery process units.

The dry gas meter was a Rockwell Model 1755 Test Gas Meter with a Number 83 Test Index.

Other equipment in the trains includes Whitey valves, copper and stainless steel tubing, Teflon hose, 100 cc glass airtight syringe, thermometers, mercury and water manometers, a cold trap, and an air-driven diaphragm sampling pump.

The leak source is shown as a valve in the figures. However, the same sampling train was used for all baggable source sampling with the flow-through technique. The size and shape of the leak source enclosure (tent) was changed and adjusted to fit each particular source shape and operating condition.

When the sampling train is operating, the vacuum pump is able to maintain a maximum flow rate of approximately two and one-half cubic feet per minute.

Sample bags were used to collect gas samples and transport them to the mobile laboratory for analyses. Several types of bags were tested by Radian in the laboratory and in the field. Most of them, including Calibrated Instrument

Company's five-layer "snout" bags, were found to adsorb hydrocarbons, making them unsuitable for use. Bags of 2 mil Mylar and Tedlar plastic were constructed, and were found to be very satisfactory. A drawing of a typical sample bag is shown in Figure A2-13.

A cold trap was placed in the system to condense water and heavy hydrocarbons, thus preventing condensation in downstream lines and equipment. The cold trap was simply a 500 ml flask in an ice bath and was placed as close as possible to the tent. This ice bath was found to be very effective in preventing condensation in the remainder of the sampling train and in the gas sample bag. Any organic condensate that collected in the cold trap was measured and recorded for later use in calculating total leak rates. The use of such a cold trap is critical; without it, order of magnitude errors are possible and, in some cases, probable.

2.1.4 Tent Construction

An enclosure or tent of Mylar plastic (polyethylene terephthalate) is formed around the leak source. The thickness of the Mylar can range from 1.5 - 15 mil depending on the type of source being bagged. Radian has found that Mylar is well suited to this function as it does not absorb significant amounts of hydrocarbons, it is very tough, and it has a high melting point (250°C). A typical tent is shown in Figure A2-14.

The enclosures were kept as small as practical. This had several beneficial effects:

- The time required to reach equilibrium was kept to a minimum.

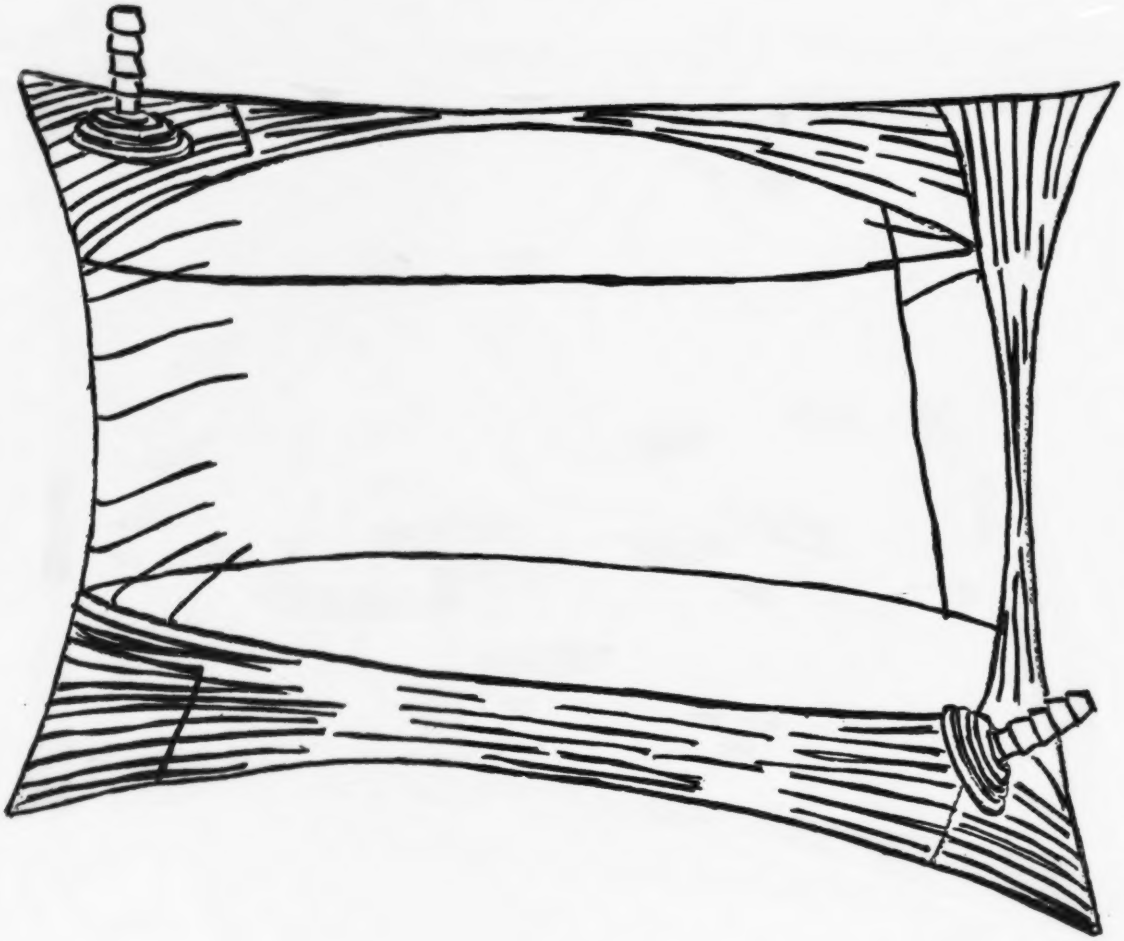


Figure A2-13. Mylar Plastic Sample Bag

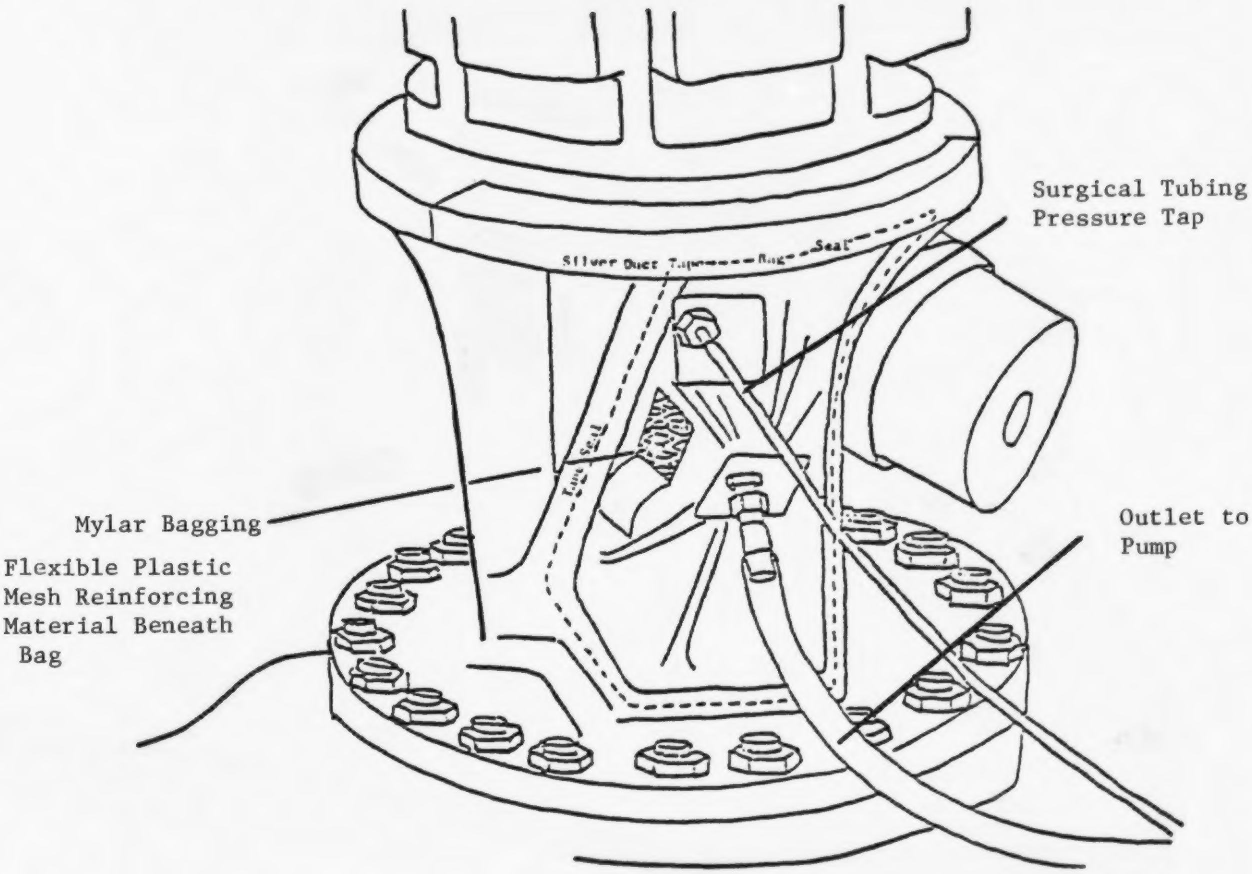

Surgical Tubing Pressure Tap
Silver Duct Tape
Bag Seal
Tape Seal
Mylar Bagging
Flexible Plastic Mesh Reinforcing Material Beneath Bag
Outlet to Pump

Figure A2-14. Tent Construction Around the Seal Area of a Vertical Pump

- The time required to construct the enclosure was minimized.

- A more effective seal resulted from the reduced seal area.

- Condensation of heavy hydrocarbons inside the enclosure was minimized or prevented due to reduced residence time and decreased surface area available for heat transfer.

In a typical sampling operation, the tent was constructed around the leak source and connected by means of the bulkhead fitting and Teflon hose to the sample train.

A separate line was connected from the tent to a magnahelic. This allowed continuous monitoring of the pressure inside of the tent. If a significant vacuum existed inside the tent when air was being pulled through, a hole was made in the opposite side of the tent from the outlet to the sampling train. This allowed air to enter the tent more easily and thus reduced the vacuum in the enclosure. In practice, it was found that only a very slight vacuum (0.1 in. H_2O) was present in the tent during most of the sampling, even in the absence of a hole through the tent wall. Sufficient air enters around the seals to prevent the development of a significant vacuum in the tent.

Tent construction for individual sources is discussed below:

Valves

One of the most numerous of the baggable sources to be examined in refineries was valves. Radian generally found them to be a relatively easy source to sample.

All valves were sampled in the same general manner. The principle difference was that a greater degree of care was taken in sampling control valves so that there was no possibility of interfering with the control valve mechanism or operation during the sampling interval. This was not as critical when sampling block valves, because these normally remained in a fixed position during the sampling effort.

The most important property of the valve affecting the type of enclosure (tent) selected for use is the metal skin temperature existing in the area enclosed by the tent and around which the seal is made.

At skin temperatures of 400°F or less, the valve stem and/or stem support was wrapped with 1.5 - 2.0 mil Mylar plastic and sealed at each end and at the seam with duct tape. A leak-tight seal is not required when the flow-through method of leak measurement is used. Indeed, it is better to allow for some areas of incomplete sealing to provide access for air being drawn through the tent by the vacuum pump in the sampling train.

Two bulkhead fittings are attached to the Mylar tent. One is for the water manometer or differential pressure gauge connection, and the other is for the line to the sampling train. If, after starting the sampling, a vacuum > 0.5 inch of water was found to exist in the tent, a hole was added on the side of the tent opposite the outlet to the sampling train. This provided an additional entrance for the dilution air, and the vacuum in the tent was reduced while sampling.

The Mylar tent was constructed to enclose the valve stem seal and the packing gland seal. The bonnet flange was not enclosed since this source was considered as a flange.

When skin temperatures in excess of 400°F were detected on a valve which was sampled, alternate methods of tenting the valves were used. In one method, asbestos insulating tape was wrapped around all hot points which were in contact with the Mylar tent material. Seals were then made against the insulation using duct tape or adjustable metal bands of stainless steel.

At extremely high temperatures, metal foil was wrapped around the valve leak area. Seals were made using adjustable metal bands in most cases. Occasionally, at points where the shape of the equipment prevented a satisfactory seal with metal bands, the foil was crimped against the seal sites to make a seal. It was necessary, in some of these instances, to use a relatively high capacity vacuum pump to insure a constant inflow of air through all seal areas.

Mixed-phase valve leaks were handled with the same type of enclosures described above. The leaking liquid was collected at a purposely-formed low point in the tent. This liquid rate was measured over the sampling period.

Pumps

As with valves, the property of most concern when preparing to sample a pump was the metal skin temperature at areas or points that were in contact with the tent material.

At skin temperatures below 400°F, Mylar plastic and duct tape are satisfactory materials for use in constructing a tent around a leaking pump seal. The vast majority of centrifugal pumps in refineries have a housing or support that connects the pump drive (or bearing housing) to the pump itself. The two supports normally enclose about half of the area between the pump and drive motor, leaving open areas on the sides. It is usually a relatively simple matter to cut panels to fit these remaining open areas. The panels were cut from 14 mil Mylar. Bulkhead fittings for the outlets to the water manometer and sampling train were placed through one Mylar panel and sealed. An opening (hole, bulkhead fitting) was made in the opposing panel, if necessary, to allow easier flow of dilution air into the enclosure around the seal.

In many horizontal pumps, there is a line from the bottom of the lower metal support to a drain. This line serves as a drain for coolant, sealant, and/or process liquid leaking from the pump seal. This line (and all other lines from the enclosure) was sealed off to avoid drawing air and hydrocarbon vapors from the drain back up to the sealed enclosures. If there is no liquid flowing through this drain line, it was plugged off. If liquid was going to the drain, a short length of hose or tubing was attached to the end of the drain line and looped upward to form an effective liquid seal.

In the cases where the supports were absent or quite narrow, a cylindrical enclosure around the seal was made such that it extended from the pump housing to the motor or support bearing. This enclosure was made completely of 14 mil Mylar, since this thickness provided considerable strength and rigidity.

Reciprocating pumps presented a somewhat more difficult tenting problem. If supports are present, the same type of two-panel Mylar tent can be constructed as that for centrifugal pumps. In many instances, however, sufficiently large supports are not provided, or the distance between pump and driver is relatively long. In these cases, a cylindrical enclosure similar to that used for centrifugal pumps was constructed. It was impractical to extend this enclosure all the way from the pump seal to the pump driver. In this case, a seal was made around the reciprocating shaft. This can usually be best effected by using heavy aluminum foil and crimping it to fit closely around the shaft. The foil was attached to the Mylar plastic of the enclosure and sealed with duct tape.

If the temperatures was too high or the potential points of contact too numerous to insulate, an enclosure made of aluminum foil was constructed. This enclosure was sealed around the pump and bearing housing using asbestos insulating tape.

In cases where liquid and vapors were leaking from a pump, the enclosures described above were used. The outlet from the tent to the sampling train was placed at the top of the enclosure and as far away from the spraying leak as practical. Thus, entrainment of the liquid into the sampling train (and cold trap) was avoided. The rate of leakage of liquid was measured by collecting it over a measured length of time. A low point was formed in the tent, and liquid was collected at that point, and its volume measured.

Compressors

In general, the same types of tents that are suitable for pumps can be directly applied to compressors. The construction and application of these enclosures have been described in the preceeding discussions of pump sampling and will not be repeated in this section.

Compressors generally handle light gases, and in many cases, the seals are enclosed. The seal enclosures are vented to the atmosphere at a high-point vent or may be vented to the blowdown/flare system.

If the seals are vented to a high-point vent, this vent line was sampled. A Mylar bag was constructed and sealed around the outlet of the vent and connected to the sampling train. The leak rate from the vented compressor seals was then measured using the normal flow-through method.

In the event that high-point vents were inaccessible, the vent lines from the compressor seal enclosures were disconnected at some convenient point between the compressor and the normal vent exit. Sampling was then done at this intermediate point.

When enclosed compressor seals were vented by means of induced draft blowers or fans, the outlet from the blower/fan was sampled. A pitot tube was used to determine the air flow rate. A sample of the outlet air was taken and returned to the mobile laboratory for methane and nonmethane hydrocarbon analysis. Ambient air samples were taken around the compressor seal enclosure area at the same time and were analyzed for hydrocarbon content. The compressor seal leak rate was determined from the knowledge of air flow rate, its hydrocarbon content, and the hydrocarbon content of the ambient air.

Flanges

All types of flanges, ranging from small-piping and valve-bonnet flanges to very large exchanger and vessel flanges, were sampled. In most cases, the physical configuration of flanges lends itself well to the determination of leak rates. For small to moderately large leaks on flanges with metal skin temperatures up to about 400°F, a narrow section of Mylar film was used to span the open distance between the two flange faces of the leaking source. The Mylar was attached and sealed to each flange with duct tape. Connections (bulkhead fittings) for the water manometer and sample train were attached to the Mylar.

When testing flanges with skin temperatures above 400°F, Mylar film and duct tape were not normally used. Instead, the outside perimeter of both sides of the flange connection was wrapped with asbestos insulating tape. Then a narrow strip of aluminum foil was used to span the opening between the flange faces. This narrow strip of material was sealed against the asbestos tape using adjustable bands of stainless steel.

Relief Valves

Relief devices in gas/vapor service generally relieve to the atmosphere through a large diameter pipe, often called a "horn," which is normally located at a high point on the unit that it serves. The horns can be easily bagged by placing a Mylar plastic bag over the opening and sealing it to the horn with duct tape. Because of the height above grade of many of these devices, accessibility to the sampling train was limited or prevented. It was sometimes possible to run a long hose from the outlet connection on the bag to the sampling train located at grade level.

Process drains have been classified as "active" or "washup" drains. The procedure for sampling is the same for both types.

Mylar plastic was used to tent the open top of the drain. This was cut to fit around any of the various pipes that may extend down into the drain. The mylar was sealed around these protuberances with duct tape. The seal around the drain edge was made with duct tape or aluminum foil. This seal was relatively loose to allow air to flow in around the edge of the drain and out through the tent connection to the sampling train.

Another connection on the drain tent was connected to a very sensitive differential pressure guage (Magnehelic). When the sampling train was operating, the vacuum inside the drain tent was monitored. The vacuum was kept to a minimum to avoid vaporizing, and thus sampling, more material from the drain than would ordinarily be present when the drain is open to the atmosphere.

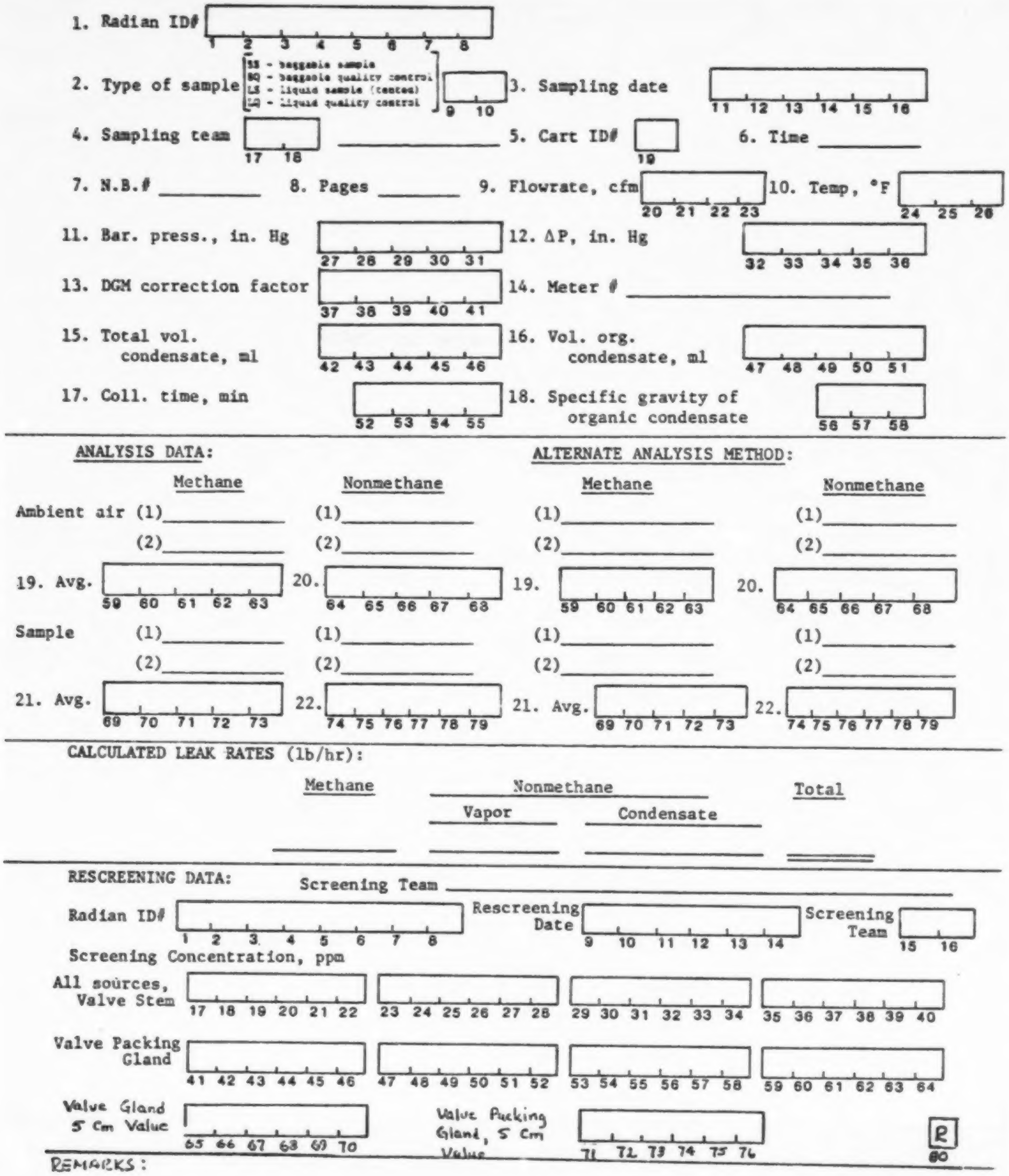
2.1.5 Sampling

The cold trap was connected to the tent and immersed in an ice bath. Then the vacuum pump was started and the timing of the run was simultaneously initiated. The time, pressure and temperature at the dry gas meter, and the dry gas meter reading, were recorded. These data were recorded at 2 - 10 minute intervals. Equilibrium was normally reached within five minutes or less. Sampling was not started until equilibrium had been established throughout the system.

The TLV Sniffer was placed in the sample train at the exit of the vacuum pump. The instrument was used to monitor the gas stream in order to assure that equilibrium had been established.

To sample the gas stream, an evacuated Mylar sample bag, which had been previously completely flushed with air for an extended period at the mobile laboratory, was attached to a three-way valve in the sampling line. A 500-ml air-tight gas syringe was used to withdraw gas samples from the sampling train. The syringe and bag were first completely flushed with sample gas. Then a sample was drawn very slowly (to avoid altering the flow rate through the tent) from the system and transferred to the bag by means of the three-way valve. This operation was repeated until the sample bag was full (5 - 7 liters). Alternately, air samples were taken using a small air-driven vacuum pump.

At the same time that this sample was being withdrawn, an ambient air sample was taken near the tent. This air sample was taken with a large plastic syringe and transferred to a Mylar sample bag. The gas sample, data sheet (Figure A2-15) and ambient air sample were taken to the mobile laboratory for analysis. The vacuum pump was then stopped and a final set of readings recorded. The cold trap was removed from the ice bath, sealed, and sent to the laboratory for analysis. The tent



1. Radian ID# (1 2 3 4 5 6 7 8)

2. Type of sample
BS - baggable sample
BQ - baggable quality control
LS - liquid sample (tented)
LQ - liquid quality control
(9 10)

3. Sampling date (11 12 13 14 15 16)

4. Sampling team (17 18) ____________ 5. Cart ID# (19) 6. Time ________

7. N.B.# ________ 8. Pages ______ 9. Flowrate, cfm (20 21 22 23) 10. Temp, °F (24 25 26)

11. Bar. press., in. Hg (27 28 29 30 31) 12. ΔP, in. Hg (32 33 34 35 36)

13. DGM correction factor (37 38 39 40 41) 14. Meter # ________________

15. Total vol. condensate, ml (42 43 44 45 46) 16. Vol. org. condensate, ml (47 48 49 50 51)

17. Coll. time, min (52 53 54 55) 18. Specific gravity of organic condensate (56 57 58)

ANALYSIS DATA: / ALTERNATE ANALYSIS METHOD:

	Methane	Nonmethane	Methane	Nonmethane
Ambient air	(1)________	(1)________	(1)________	(1)________
	(2)________	(2)________	(2)________	(2)________
	19. Avg. (59 60 61 62 63)	20. (64 65 66 67 68)	19. (59 60 61 62 63)	20. (64 65 66 67 68)
Sample	(1)________	(1)________	(1)________	(1)________
	(2)________	(2)________	(2)________	(2)________
	21. Avg. (69 70 71 72 73)	22. (74 75 76 77 78 79)	21. Avg. (69 70 71 72 73)	22. (74 75 76 77 78 79)

CALCULATED LEAK RATES (lb/hr):

Methane	Nonmethane Vapor	Nonmethane Condensate	Total
________	________	________	________

RESCREENING DATA: Screening Team ____________________

Radian ID# (1 2 3 4 5 6 7 8) Rescreening Date (9 10 11 12 13 14) Screening Team (15 16)

Screening Concentration, ppm

All sources, Valve Stem (17 18 19 20 21 22) (23 24 25 26 27 28) (29 30 31 32 33 34) (35 36 37 38 39 40)

Valve Packing Gland (41 42 43 44 45 46) (47 48 49 50 51 52) (53 54 55 56 57 58) (59 60 61 62 63 64)

Valve Gland 5 Cm Value (65 66 67 68 69 70) Valve Packing Gland, 5 Cm Value (71 72 73 74 75 76) R (80)

REMARKS:

Figure A2-15. Data Sheet - Baggables and Tented Liquid Leaks

was then removed from the source, and the train moved to the next sampling point.

Baggable Sources - Procedure for Large Vapor Leaks

Radian refinery sampling experience has shown that large vapor leaks are occasionally encountered. These leaks are so large that very high concentrations of hydrocarbon are found in the gas samples. Since the Byron THC Analyzer cannot measure concentrations above 20,000 ppm, considerable dilution of the sample was required in order to obtain a diluted gas concentration in the proper range.

In some cases, a leak may be large enough to exceed the capacity of the vacuum pump. This leads to a pressure buildup in the tent and sampling train. Ultimately, leakage around seals or rupture of the tent occurs. In any event, erroneous results are obtained.

When large leaks are encountered, direct measurement of the hydrocarbon vapor rate is the quickest and most reliable method of determining the leak rate. In these cases, the vacuum pump is disconnected from the sampling train. The gas from the leak source is allowed to pass through the sampling train (including the cold trap) and exit to the atmosphere immediately downstream of the dry meter. After equilibrium has been established, the flow rate through the dry gas meter is a direct measure of the hydrocarbon vapor leak rate.

There are some precautions which must be taken when applying this sampling method. Since there is a slight positive pressure (instead of the slight vacuum obtained with the flow-through method), the tent seal must be leak-free. The tent seals can be checked for leakage with soap solution (in the case of cool sources) or the TLV Sniffer can be used to detect leakage by passing the probe along all tent seals.

The measured quantity in this sampling method is normally the volume of hydrocarbon leaking from the source. In order to determine the weight of gas leaking from this source, the composition and/or molecular weight of the gas must be known. This can be determined from either the process information available from the refinery or from an analysis of the gas with a gas chromatograph. The mobile laboratory was equipped with such an instrument.

Baggable Sources - Procedure for Liquid Leaks

For the purpose of this discussion, liquid leaks are defined as those leaks from which only liquid is observed to escape. This means that vapor leaks are neither observed visually nor are they indicated by TLV Sniffer readings of 200 ppm or more at the immediate point of leakage. If the liquid was of such a volatility as to vaporize rapidly and completely in the vicinity of the escape point, it was treated as a vapor leak and bagged.

When a liquid leaks from a source, and some sort of equilibrium has been established such that there is no net accumulation at any point, there are basically only three places for this liquid to go.

(1) it can vaporize into the atmosphere,

(2) it can be absorbed into the ground, and

(3) it can enter the wastewater system through drains, sewers, or ditches.

Generally, the fate of the liquid is a combination of two or three of the above possibilities. The more common probabilities in refineries are (1) and (3). Since the thrust of this program is aimed at the quantification of emissions to the air, some means must be used to measure and/or estimate the amount of material that is ultimately vaporized.

In order to measure the liquid leak rate at the source, the material was collected in a graduated container. In the case of hot and/or volatile liquids, the graduated container was externally cooled with ice and fitted with covers to contain most of the material. Flow rates were determined at the leak site by measuring the change in volume with respect to time.

If the material is not absorbed into the ground or does not enter the wastewater system, it will all be vaporized unless a continuous accumulation is occurring. If there was no net accumulation, the amount being vaporized was assumed to be equal to the measured liquid leak rate.

Baggable Sources - Procedures for Multiphase Leaks

Multiphase leaks in which one is a liquid hydrocarbon and others are water and/or water vapor were primarily associated with pumps and compressors which have water or steam-jacket devices and drains. The water was condensed and trapped in the cold trap and did not interfere with hydrocarbon analysis of the bagged gas.

2.2 Nonbaggable Sources

There are a number of potential hydrocarbon emission sources in a refinery that are not amenable to sampling with bags or enclosures. These sources include operations that are broad in area, intermittant in operation, and/or very complex in their functioning.

Nonbaggable sources include drainage and wastewater systems, cooling towers, barometric condensers, removal of coke from delayed cokers, sampling operations, blind changing, and maintenance turnarounds. Some of these sources can only be sampled using very elaborate and complex sampling procedures and equipment. The sampling of the nonbaggable sources that could be reasonably sampled will be described in this section. These sources are the wastewater system and cooling towers.

2.2.1 Nonbaggable Sampling Philosophy

The approach to sampling nonbaggable systems was to use a mass balance around the particular unit. The difference between the hydrocarbon into the system (liquid influent) and hydrocarbon out (liquid effluent) is equal to fugitive emissions to the atmosphere.

The key elements to this approach are collection of representative samples of liquid streams into and out of a particular unit and accurate measurement of flow rates through the system.

Sampling of some units was not done. If the total hydrocarbon content of the water leaving a treatment unit was equivalent to or less than 200 lbs/day or 0.001 percent of the processed crude oil, whichever was smaller, the remainder of the downstream wastewater system was not tested for emissions of hydrocarbons. Even if all contained hydrocarbons were emitted as volatile hydrocarbons, the potential for emissions in the remainder of the system was still small.

Those nonbaggable sources that were sampled are discussed in the following section.

2.2.2 Nonbaggable Source Sampling

Oil-Water Separators

Oil-water separation is normally the first process that the wastewater encounters as it enters the wastewater treatment section of a refinery. Oil-water separation can be accomplished in a surge tank, API separator, or corrugated-plate interceptor. The API separator is the most widely used of these three types of separators. The sampling methods described below for API separators can be applied to the other two types of units, also.

The inlet liquid to the separator consists of a mixture of hydrocarbon and water. The principal problem encountered in sampling is the procurement of truly representative samples of two-phase streams. Samples of each phase were obtained from the separator inlet line, or from the separator at a point as close as possible to the oil-water inlet.

Three streams normally exit from an API separator. These are the oil that is skimmed from the surface of the liquid in the separator, the water, and sludge that is pumped from the bottom of the separator. The sludge was not considered in the sampling program. It was assumed to contain low levels of volatile compounds and to settle to the bottom. Oil layer samples were centrifuged to remove sludge particles before analysis.

The oil that is skimmed from the surface of the separator is normally pumped to a slop-oil tank. Oil samples were preferably taken at the outlet of this pump to insure a reasonably representative sample. Other sampling points were the skim pipe itself, the line from the separator to the slop tank, and the slop tank itself.

In the separator the water flows under a barrier weir and then over another weir to a basin from which it is pumped or allowed to flow by gravity to the next processing area in the wastewater treatment. Water samples were taken at the overflow weir. Samples were obtained at several points along the weir, and were composited to form one sample. Factors which determined the particular sampling point for a given separator included accessibility, residence time in the basin, and presence of sample taps in the pump discharge line.

The average oil outlet rate can be determined from level readings on the slop-oil tank over given periods of time. The average outlet oil rate was used to estimate the residence time in the API separator. The thickness of the oil layer in the separator, and the dimensions of the area containing the oil layer also are required in estimating the oil residence time.

Samples were taken of each stream at each separator several times a day for several days. Daily samples from each sample point were composited before analysis. The oil and water samples from the inlet and outlet of the API separator were collected in glass bottles. These bottles were completely filled and kept tightly capped to prevent the escape of volatile hydrocarbons.

Dissolved-Air Flotation Units

If dissolved-air flotation (DAF) units are used in a refinery wastewater treating system, they usually process water from the oil-water separators. Air is dissolved or sparged into the water, and the air bubbles attach themselves to colloidal oil droplets, causing them to rise to the surface, where the oil-air emulsion is removed.

Some DAF units are partially enclosed and others are completely open to the atmosphere. The hydrocarbon material balance method is the selected technique for determining hydrocarbon emissions from open units, and may also be used for partially enclosed units.

Only one stream containing a significant amount of hydrocarbons enters the DAF unit. This is the water phase from the oil-water separator. There is normally little free oil in this water. Ambient air, which may contain low background concentrations of hydrocarbons is also injected or sparged into the water. Three streams leave the DAF unit. These are the water, the air-oil emulsion and air. All these streams contain some hydrocarbons.

When applying the material balance method to DAF units, samples of inlet water were taken. These were normally the same as the outlet water samples from the API separator, and the same analysis sufficed for both separator and DAF hydrocarbon material balances.

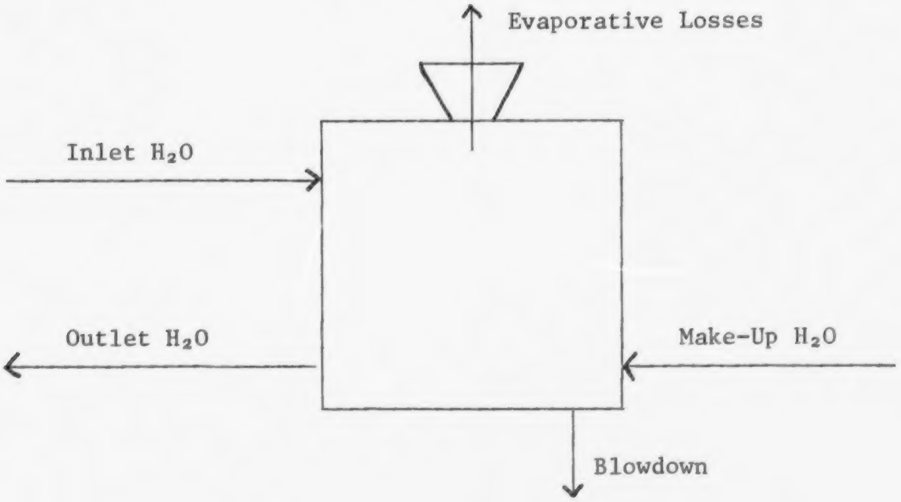
In order to close the material balance sufficiently to calculate hydrocarbon emissions, samples of the outlet water stream and the air-oil emulsion must also be taken. The outlet water sample was taken at the overflow weir. The emissions from air-oil emulsion samples were judged to be negligible contributors to air emissions.

The water samples were collected several times each day for several days. The daily samples from each point were composited for analysis.

Cooling Towers

The selected method for determining hydrocarbon emissions from cooling towers is the hydrocarbon material balance. Water enters the cooling towers from two sources: make-up water and the hot water from process exchange. Water, in significant quantities, leaves as vapor from the top of the cooling tower, as cooled water returning to process exchange, and as blowdown. A water material balance shows that the outlet rate to the process must equal the inlet water rate from the process, since the make-up water rate is controlled to exactly balance blowdown plus evaporation.

Thus, if the hydrocarbon content of the incoming hot water and the return cooled water are known, the evaporative hydrocarbon emissions can be determined. This is shown in Figure A2-16.


Evaporative Losses
Inlet H_2O
Outlet H_2O
Make-Up H_2O
Blowdown

$$HC_{In\ H_2O} + HC\overset{0}{\nearrow}_{MU\ H_2O} = HC_{Out\ H_2O} + HC_{BD} + HC_{Evaporation}$$

or

$$HC_{Evaporation} = (HC_{In\ H_2O} - HC_{Out\ H_2O}) - HC_{BD}$$

or to be specific:

$$\text{Evaporative Emissions} = (\text{Circulation, GPM})(8.33\ \frac{\text{lb}}{\text{gal}})(\text{ppm}_{in} - \text{ppm}_{out})(10^{-6})(60)$$

$$- (\text{Blowdown, GPM})(8.33)(60)(\text{ppm}_{out})(10^{-6})$$

Figure A2-16. Mass Balance Around a Cooling Tower

Samples of inlet and outlet cooling water were collected daily from each selected tower over a period of several days. In order to diminish the effect of hydrocarbon concentration fluctuations, the outlet sample was taken from the water flowing downward through the tower at a location just above the level of the cooling tower basin. The inlet samples were taken from one of the many small sampling valves which are normally present and branch off the large cooling water return risers. Many of these are continually flushed into the tower basin. The hydrocarbon content of the blowdown stream was assumed to be the same as that of the outlet water stream.

The samples were kept in sealed bottles under refrigeration until they were analyzed.

3.0 STACK SAMPLING

Stacks or vents which can be identified as emission points for hydrocarbons and other criteria pollutants are classified as process sources. These process sources can be divided into seven categories:

- catalytic cracking unit regenerator stacks,
- boilers and process heater stacks,
- sulfur recovery unit or tail gas treating unit stacks,
- compressor engine exhausts,
- flares and blowdown systems,
- vacuum jet vents, and
- air blowing.

The general strategy regarding the sampling of point source emissions included sampling the total hydrocarbon emissions, obtaining samples for speciation analysis and sampling for other criteria pollutants. The methods employed by Radian for the measurement of stack emissions are discussed in a subsequent section.

The magnitude of the required process source sampling depended on the size and configuration of the individual refineries as well as the amount of valid data available at each.

As a base case, data were taken on one catalytic cracking unit regenerator stack, one sulfur recovery or tail-gas treating unit stack, and two process heater stacks.

Measurements made in the base case were: EPA Reference Methods No. 1, 2, 3, 4, and 5 on all stacks;[7] methane and nonmethane hydrocarbons on all stacks; particulate and vapor collection for organic characterization on one stack; and, sulfur gases on the sulfur recovery and/or tail-gas treating stack.

There were four types of changes to the base case:

- sampling for additional stacks (larger refineries),
- sampling of fewer stacks (smaller refineries),
- sampling the base case stacks for additional species, or
- any combination of 1 or 2, and 3 above.

3.1 Process Source (Stack) Sampling - Sampling Trains

Stack sampling procedures are a combination of: EPA approved methods[7] for criteria pollutants (SO_2, SO_3, and particulates); EPA Level 1[7] screening procedures (SO_2, COS, CS_2, H_2S, NO, NO_x, "organic vapor," and Radian-devised methods (HCN, NH_3, THC). The procedures were selected with several criteria in mind:

- accepted or proved methodology,
- accurate, reproducible measurements,
- commercially available equipment,
- freedom from interference,
- cost-effective trade-off between sampling and analysis, and
- shortest feasible sampling time.

Figures A3-1 through A3-3 depict the sampling trains used.

3.2 Stack Sampling Methods

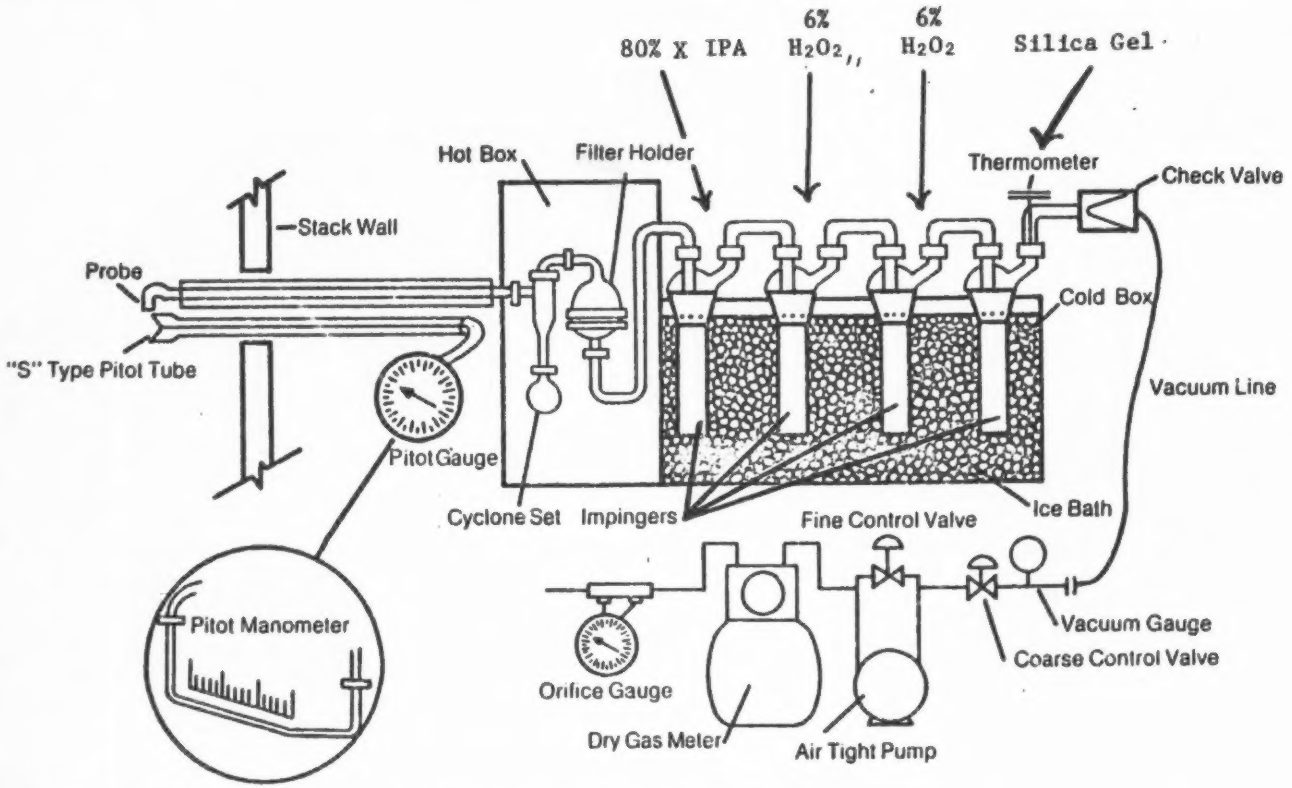
The characterization of refinery stack emission involved sampling and analysis for the following species:

particulates
SO_x
trace organic species
total aldehydes
total hydrocarbons
fixed gases
sulfur species
nitrogen species

The following paragraphs will detail Radian's sampling methods for each of the above categories of pollutants. A discussion of sampling schedules and frequency is also included. The methods used for analysis of these species will be detailed in a later section.

3.2.1 Particulates

Particulate samples were collected from each stack according to the procedure described in the EPA Reference Method 5[7] using a Lear Sigeler, Inc. stack sampling train. Sampling


80% X IPA
6% H2O2
6% H2O2
Silica Gel
Hot Box
Filter Holder
Thermometer
Check Valve
Stack Wall
Probe
"S" Type Pitot Tube
Cold Box
Vacuum Line
Pitot Gauge
Cyclone Set
Impingers
Fine Control Valve
Ice Bath
Pitot Manometer
Vacuum Gauge
Coarse Control Valve
Orifice Gauge
Dry Gas Meter
Air Tight Pump

Source: Lear Siegler, Inc., PM 100 - Operation & Maintenance Manual.

Figure A3-1. Method 5 Train for SO_2 and Particulates

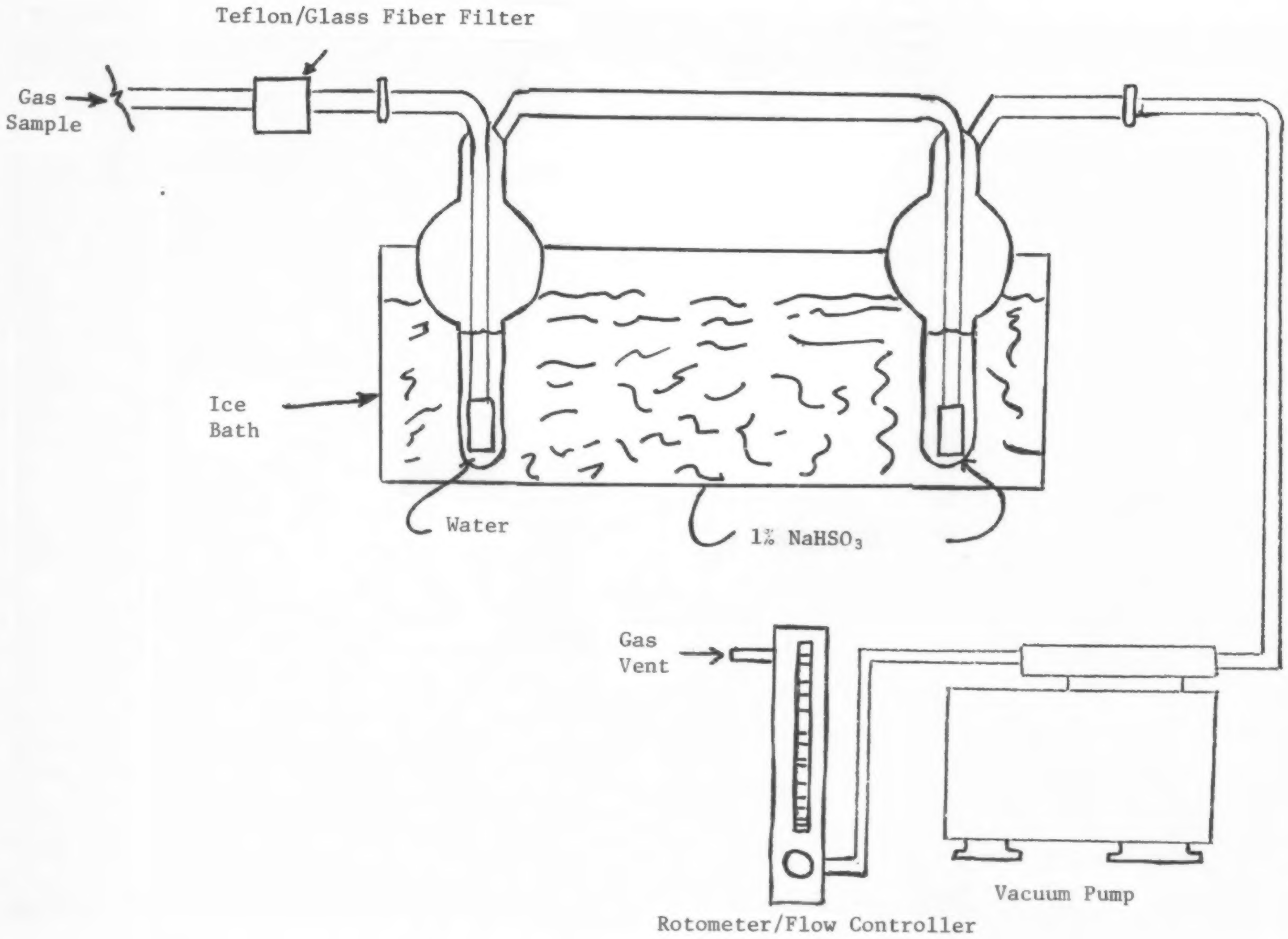

Teflon/Glass Fiber Filter
Gas Sample
Ice Bath
Water
1% $NaHSO_3$
Gas Vent
Rotometer/Flow Controller
Vacuum Pump

Figure A3-2. Aldehyde Impinger Train

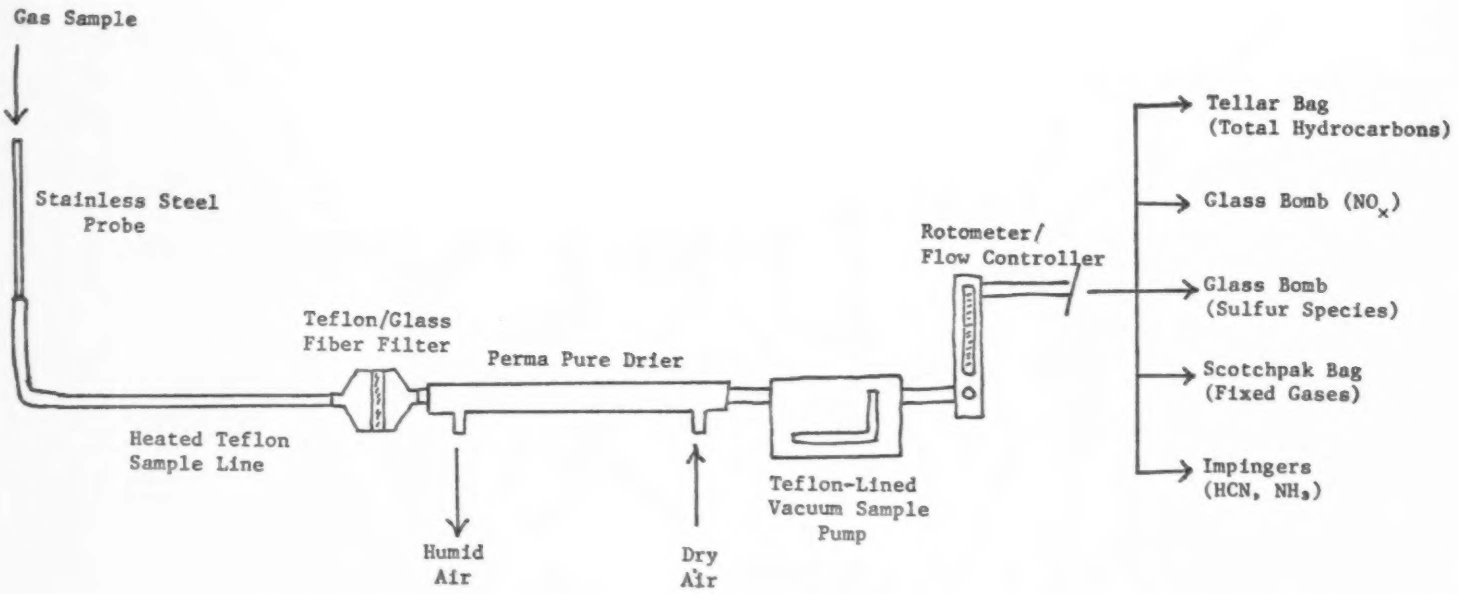

Gas Sample
Stainless Steel Probe
Heated Teflon Sample Line
Teflon/Glass Fiber Filter
Perma Pure Drier
Humid Air
Dry Air
Teflon-Lined Vacuum Sample Pump
Rotometer/ Flow Controller
Tellar Bag (Total Hydrocarbons)
Glass Bomb (NO_x)
Glass Bomb (Sulfur Species)
Scotchpak Bag (Fixed Gases)
Impingers (HCN, NH_3)

Figure A3-3. Grab Sample Collection and Preparation System

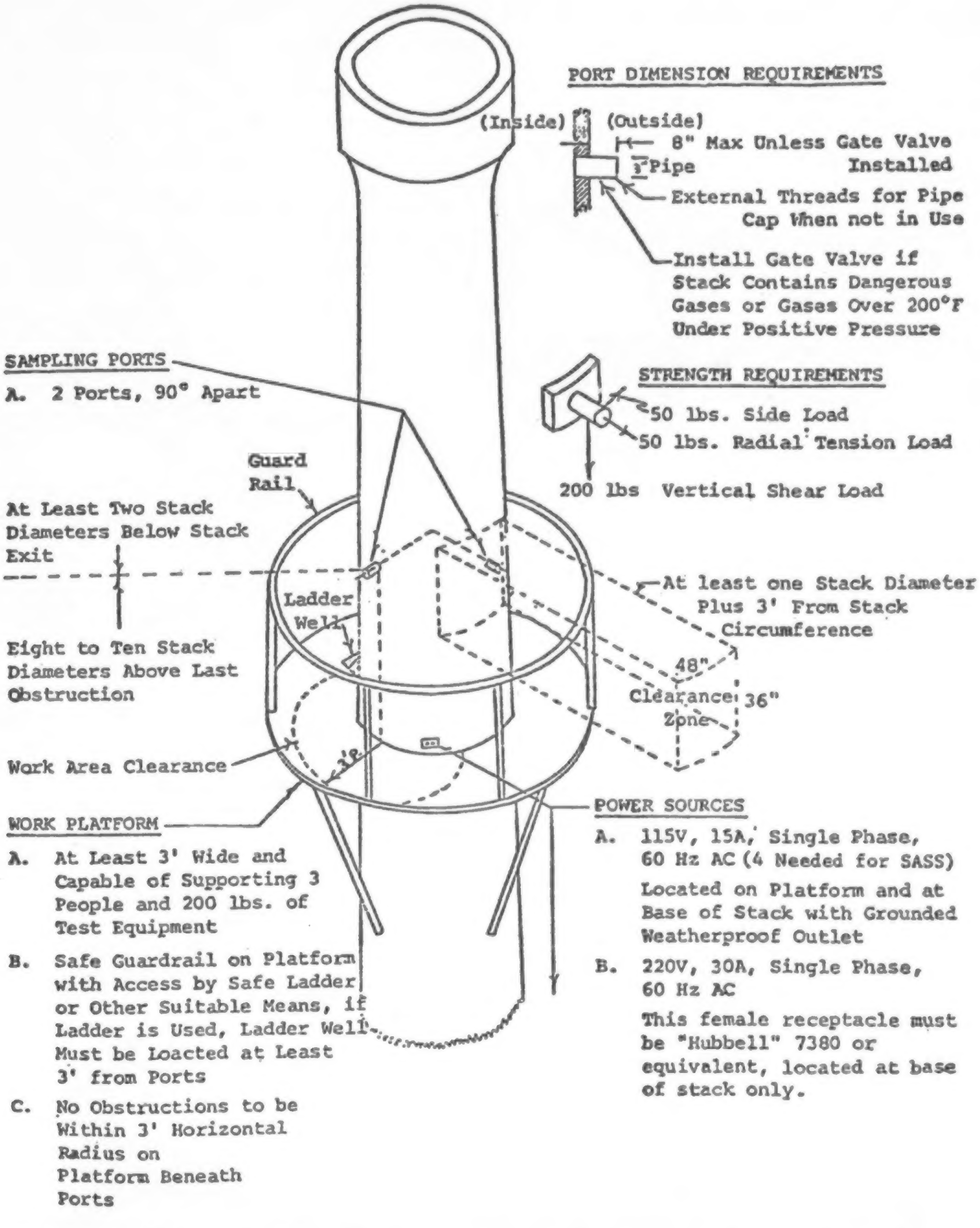
was performed isokinetically along two perpendicular traverses of each stack. Duplicate sample runs were made on each stack insofar as possible. Stacks were sampled that did not meet Reference Method guidelines for port location. In those cases the number of traverse points were taken that were felt to be useful. Figure A3-4 shows the points evaluated on inspection trips to select stacks to be sampled.

3.2.2 SO_x

Oxides of sulfur (SO_3 and SO_2) were collected according to EPA Reference Method 8. This was done during each particulate collection run by passing the filtered sample gases through an impinger train consisting of an 80 percent isopropanol impinger for SO_3 followed by two 6 percent aqueous hydrogen peroxide impingers for SO_2 and a silica gel impinger. The total mass of water collected in this train was used to determine the moisture content of the stack gas.

3.2.3 Aldehydes (A)

The aldehyde train (Figure A3-2) used in sampling stacks consisted of two ice-cooled impingers, each containing 10 ml of a 1.0 percent aqueous sodium bisulfite solution. Approximately, 12 liters of stack gas were drawn through each impinger train at a rate of 200 ml per minute. A stainless steel probe was inserted into the stack to a point of average velocity, and the gas was transferred to the impinger train by a small vacuum sampling pump through a heated Teflon sample line equipped with a Teflon particulate filter. Radian has found that the use of a heated transfer line is very important to prevent moisture condensation and subsequent loss of sample by absorption and dissolution.


(Inside)
(Outside)
8" Max Unless Gate Valve Installed
3" Pipe
External Threads for Pipe Cap When not in Use
Install Gate Valve if Stack Contains Dangerous Gases or Gases Over 200°F Under Positive Pressure
50 lbs. Side Load
50 lbs. Radial Tension Load
200 lbs Vertical Shear Load
Guard Rail
At Least Two Stack Diameters Below Stack Exit
Eight to Ten Stack Diameters Above Last Obstruction
Ladder Well
At least one Stack Diameter Plus 3' From Stack Circumference
48"
36"
Clearance Zone
Work Area Clearance
3'

PORT DIMENSION REQUIREMENTS

STRENGTH REQUIREMENTS

SAMPLING PORTS

A. 2 Ports, 90° Apart

WORK PLATFORM

A. At Least 3' Wide and Capable of Supporting 3 People and 200 lbs. of Test Equipment

B. Safe Guardrail on Platform with Access by Safe Ladder or Other Suitable Means, if Ladder is Used, Ladder Well Must be Loacted at Least 3' from Ports

C. No Obstructions to be Within 3' Horizontal Radius on Platform Beneath Ports

POWER SOURCES

A. 115V, 15A, Single Phase, 60 Hz AC (4 Needed for SASS)
Located on Platform and at Base of Stack with Grounded Weatherproof Outlet

B. 220V, 30A, Single Phase, 60 Hz AC
This female receptacle must be "Hubbell" 7380 or equivalent, located at base of stack only.

Figure A3-4. Refinery Inspection Trip - Refinery Stack Facilities Summary

Aldehydes (B)

A second impinger sampling train was sometimes used to sample for total aldehydes. It consisted of three ice-cooled impingers, the first containing 10 ml water and the following two containing 10 ml of 0.05 percent aqueous 3-methylbenzothiazolone-hydrazone (MBTH) solution. The aldehydes were collected by dissolution in the water and reaction with MBTH to form a water-soluble adduct. Approximately 12 liters of stack gas were drawn through the impinger train at a rate of 200 ml per minute. Radian has also found that when sampling combustion gases, it is often necessary to protect the MBTH impingers by first passing the gas through a water impinger to scrub out as yet unknown compounds which destroy the MBTH. As a safety precaution, the scrubber impinger was used during all sampling runs. The aldehydes collected in this impinger were determined by adding MBTH to the solution after the sampling run and analyzing on-site as with the other impinger solutions.

3.2.4 HCN and NH_3

Hydrogen cyanide was collected using the Method 5 stack sampling equipment by passing the filtered sample gases through three impingers containing 2.0 N sodium hydroxide. Ammonia was collected similarly using three impingers containing 0.1 N sulfuric acid. In each case sampling was conducted over thirty-minute periods and resulted in approximately 10 SCF of gas for each sample.

3.2.5 Grab Samples

The remaining four categories of species are all collected by grab sampling techniques. From Radian's experience in sampling for these species in refinery stack gases, it has been found that collecting and transporting the sample in a way that preserves its integrity is a nontrivial task. All of the following factors have been found to contribute to the nonrepresentativeness and/or degradation of the sample:

- sampling equipment construction,
- condensation of moisture in the sample line and vessel,
- particulate removal,
- sample vessel construction, and
- time lag between sampling and analysis.

Radian has developed a sampling system and operating procedure which eliminate the negative aspects of all five of the above factors. A stainless steel probe is inserted into the stack to the point of average velocity, and the sample gas is drawn out through a heated Teflon sampling line. The construction of the sample line is important to prevent moisture condensation and reaction of the reactive species with any noninert surfaces. The sample then passes through a heated Teflon glass/fiber filter to remove particulates followed by a permeation drying system to remove moisture. The Perma-Pure Products, Inc. multi-tube drier has been found to be effective in removing moisture down to < 100 ppm while causing only a 1 to 3 percent loss of the desired species. Without this sample drying technique, condensation of moisture inside the sample vessels and the resulting reaction, absorption or dissolution of reactive species has resulted in poor analyses and complete loss of sample. Movement of the sample through the system is accomplished by a miniature Thomas vacuum pump equipped with Teflon heads and diaphragm. The outlet stream from the pump is directed to the several bags and bombs used to transport the samples to the field laboratory for analysis. Sampling and analysis procedures allow no more than 15 minutes elapsed time between sample catch and start of analysis. If the sample was not analyzed within that time, a new sample was obtained.

3.2.5.1 Hydrocarbons

Samples for methane and nonmethane hydrocarbon analysis were collected in 4 liter Tedlar sample bags. Bags made of aluminized polyethylene have been tried, but substantial sample loss through absorption or reaction was observed. The Tedlar bags were flushed with zero grade air prior to use.

3.2.5.2 Fixed Gases

Samples for fixed gases (CO_2, N_2, H_2, O_2, CO) analysis were collected in aluminized Scotchpak sample bags. These species are quite unreactive and are not prone to absorb onto the bag walls significantly.

3.2.5.3 Gaseous Sulfur Species

The sulfur species, CS_2, H_2S, COS, and SO_2, proved to be the most difficult to collect and transport. The two major problems of reaction/dissolution with condensed moisture and reaction/absorption on the surfaces of the sample vessel were eliminated by using the sample system (150 ml glass bomb) described in Figure A3-3.

3.2.5.4 $\underline{NO_x\ (A)}$

Samples for NO_x were collected in evacuated 2 liter glass flasks to which had been added 25 ml of a potassium dichromate-aqueous sulfuric acid solution. The temperature and pressure of the gas were recorded.

3.2.5.5 $\underline{NO_x\ (B)}$

Samples for NO_x were collected in evacuated 2 liter glass flasks to which had been added 15 ml of chromotropic acid solution. The temperature and pressure of the gas were recorded.

This method was finally used exclusively because it appeared to be more reliably accurate than the method described in Section 3.2.5.4.

4.0 SPECIES IDENTIFICATION

4.1 Sampling Strategy

4.1.1 Speciation Source Selection

During the sampling for total hydrocarbon emissions a minimum number of process streams, process emissions, and flue gas streams were sampled for complete characterization. The sources were selected for sampling because of their importance/ distribution in the refineries and/or their potential for containing some possibly hazardous compounds.

The location and number of samples collected for species identification are shown in Tables A4-1 and A4-2. Within the economic and time limitations of this program, the sampling scheme provided a reasonably complete basis for estimating the potentially hazardous compounds which might be emitted from refinery operations. Samples were taken in 13 refineries.

4.1.1.1 Vapor Liquid Compositions of Fugitive Emissions

The relationship between the composition of a vapor leak and the composition of the stream from which it came was investigated by taking both liquid and vapor speciation samples wherever possible. (This was not always possible because not every stream selected for speciation sampling contained vapor-leaking sources.)

Vapor samples for speciation analyses were taken by means of adsorption on a porous polymer. Extraction with an organic solvent released the adsorbed material for analysis.

TABLE A4-1. SPECIATION SAMPLES - PROCESS STREAMS

Process Unit	Process Stream	Number of Samples
Crude Distillation	Flashed Crude	1
	Atm. Column Overhead Accumulator Gas	1
	Intermediate Naphtha Product	1
	Full Range Straight Run Naphtha	1
	Virgin Middle Distillate Product	1
	Atmospheric Gas Oil	1
	Light Vacuum Gas Oil	1
	Vacuum Gas Oil	2
	Heavy Vacuum Gas Oil	1
	Vacuum Residuum	1
Fluid Catalytic Cracking	Low Pressure Separator Gas	2
	Low Pressure Separator Liquid	3
	Light Cycle Gas Oil	2
	Heavy Cycle Gas Oil	3
Catalytic Reforming	Recycle Hydrogen Stream	1
	Naphtha Feed	2
	Reformate Product	6
Alkylation	Crude Alkylate	3
	Product Alkylate	1
Hydrodesulfurization	Desulfurized Naphtha Product	1
	Desulfurized Gas Oil	1
Gasoline Sweetening	Mixed Naphtha Feed	1
Solvent Dewaxing	Slack Wax	1
Gas Absorption Unit	Lean Oil (Naphtha)	1
Crude Desalting	Effluent Water	3
API Separator	Surface Oil at Inlet	2
	Surface Oil at Outlet	2
Sour Water Stripper	Sour Water Feed	1

TABLE A4-2. SPECIATION SAMPLES - FLUE GAS STREAMS

Process Unit	Flue Gas Stream	Number of Samples
Fluid Catalytic Cracking	CO Boiler Outlet	5
	Flue Gas Scrubber Outlet	1
Thermofor Catalytic Cracking	CO Boiler Outlet	1
Fluid Coking	Scrubber Inlet	1
	Scrubber Outlet (CO Boiler Inlet)	2
	CO Boiler Outlet	1
Resin Fume Oxidation	Outlet	1

The effect of this technique is removal and concentration of materials in the hydrocarbon/air mixture.

4.1.1.2 Liquid Samples

Liquid samples taken as speciation samples were drawn directly from sample lines or ports. In some cases, it was necessary to pass hot liquid through a cooling coil in an ice bath as it came out of the line. In this manner, vaporization of the more volatile constituents was prevented.

4.1.2 Flue Gas Emissions

At each refinery one gas source sample and one particulate sample were taken from either an FCCU regenerator stack or CO boiler stack. If more than one FCCU unit were available at some sites and none were available at others, more samples were taken at the site with multiple FCCU's.

4.2 Sampling Methodology

4.2.1 Sorbents

For broad boiling range speciation a combination of sorbent techniques is advisable. For volatile organics from acetone to naphthalene, Tenax can be used as a sorbent and thermally desorbed. Benzenes, toluenes and xylenes are the compounds in the volatility range that would be expected as fugitives with known adverse environmental effects. Charcoal tubes are designed to trap components in and above this volatility range. Charcoal tubes are also efficient in the trapping of very volatile emissions, such as vinyl chloride, which are of interest from a health effects standpoint, but not expected as fugitives from the refining process. To provide a volatility continuum, charcoal tubes should be used in the fugitive sampling procedure and the extracts analyzed for any compounds of interest in the 120°C to 150°C boiling range. For the high molecular weight fugitives, XAD-2 is recommended as an adsorbent. Heterocyclic nitrogen and sulfur compounds and polynuclear aromatic emissions are trapped with the XAD-2 sampling module. Each sorbent system is outlined in the following sections.

4.2.1.1 Tenax Adsorbent System

The Tenax tube shown in Figure A4-1 is 1/8 inch O.D. glass-lined steel which contains approximately 0.8 cc Tenax and approximately 0.4 cc Davidson #15 silica gel. Most volatile organic species in the boiling range between acetone and naphthalene may be determined by thermal desorption from Tenax. Radian has previously measured a variety of volatile organic species including aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, ethers, esters, acrylates, ketones, chloronitriles, sulfides, mercaptans, nitriles, and alcohols by this technique. In general, 50 - 100 ng of an organic compound sorbed onto a Tenax tube will give adequate peak size for GC/MS measurement. A lower detection limit of approximately 1 ng is possible for most organic compounds. If the maximum sample capacity of the Tenax is limited by the benzene breakthrough volume of 2 liters, 50 ng of an organic compound with a molecular weight of 100 has a detection level of 6 ppb. Compounds having less hydrocarbon character, such as alcohols, have lower breakthrough volumes. Obviously then, a 1 liter sample with the same constraints yields a 12 ppb detection limit. For the light aromatics of interest however, 1 ppb is possible with a corresponding reduction in mass available for quantification.

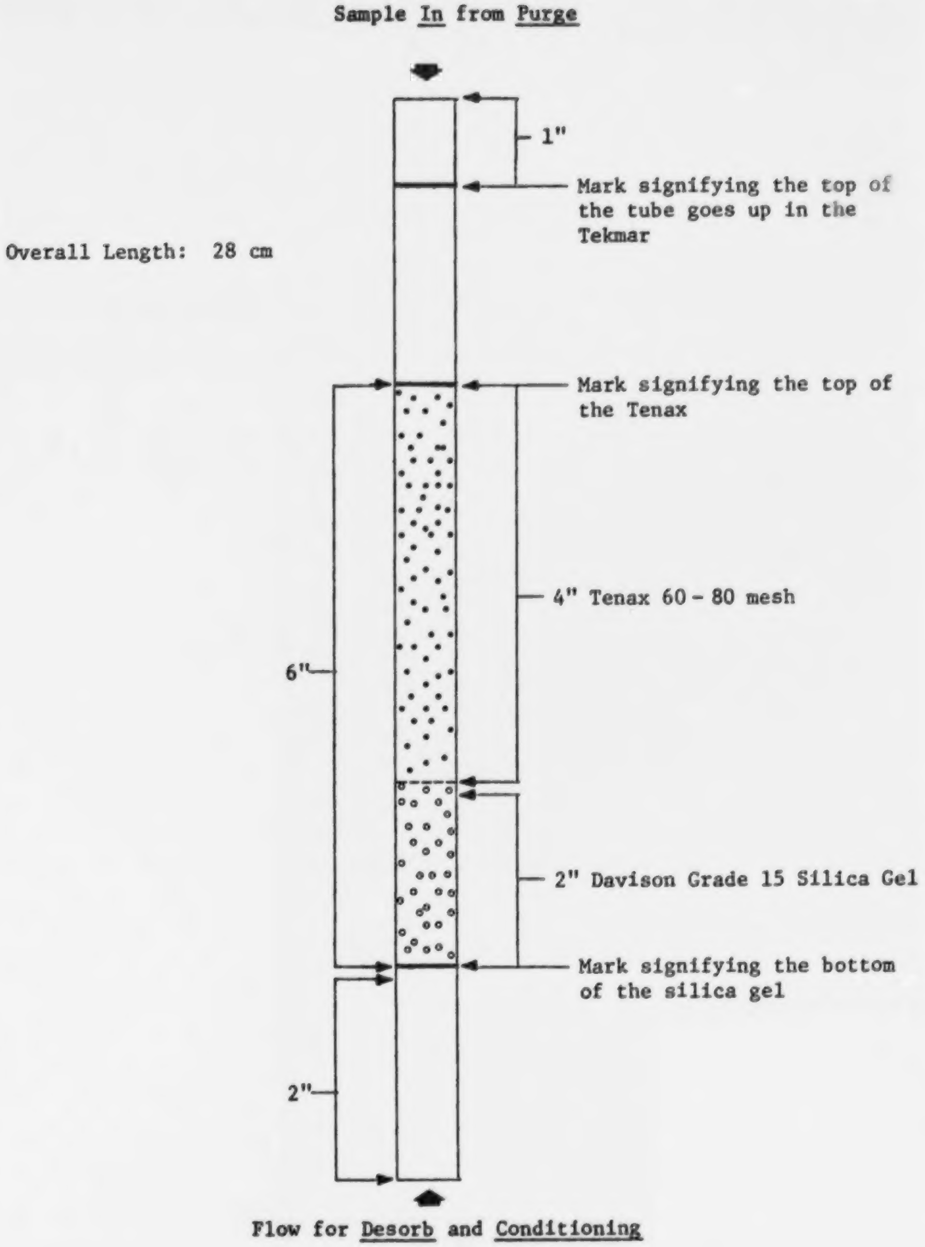

Sample In from Purge
1"
Mark signifying the top of the tube goes up in the Tekmar
Overall Length: 28 cm
Mark signifying the top of the Tenax
4" Tenax 60 - 80 mesh
6"
2" Davison Grade 15 Silica Gel
Mark signifying the bottom of the silica gel
2"
Flow for Desorb and Conditioning

Figure A4-1. Stainless Steel Glass-Lined Tenax-Silica Gel Purge Traps

4.2.1.2 Charcoal Sampling System

A NIOSH method[10] describes the collection and analysis of organic solvents in air. The regulated compounds which are determined by this method are given in Table A4-3. In Table A4-3, the standards are expressed as a time weighted average (TWA) over 8 hours of continuous exposure. The maximum concentration allowable for short time exposures, the ceiling level, is considered to be the TWA concentration if no other ceiling level has been determined. Vapors are collected with a portable personal pump at the flow rates and volumes indicated in the table. After the recommended sample has been taken, the charcoal tube is capped and stored below room temperature to reduce sample migration. The charcoal is desorbed with CS_2 in most cases. Table A4-3 also lists recommended solvents for desorption. The desorbed sample should be analyzed within 48 hours. Both the 50 mg and the 100 mg sections are analyzed. If the backup section has 10 percent or more of the quantity found on the 100 mg portion, the possibility of sample loss exists and the sample cannot be quantitated. The charcoal tubes contain 150 mg 20/40 mesh activated coconut charcoal. The front 100 mg is used for collection, the remaining 50 mg is used as backup to determine if breakthrough has occurred.

The advantages of charcoal tubes, in addition to their convenient size, is that established NIOSH parameters can be used for any compound of concern included in the table. The limitations of the method which must be considered are: (1) displacement of collected compounds by solvents present in the atmosphere which are more strongly adsorbed, (2) severe decreases in breakthrough volume due to high humidity, (3) conversion of reactive gases to other species on the carbon surface, (4) requirement of numerous tubes for monitoring

TABLE A4-3. OSHA STANDARDS AND SAMPLING PROCEDURES

Chemical With Established Procedure	● Molecular Weight (g/mole)	● Density (g/ml)	OSHA Standard		Sample Volume Liters		Sample Rate ml/min.		Sample Time		Desorp. Sol. (Eluent)	GC Column	Sample Tubes		
			TWA ppm	Ceil. ppm	Ceil.	TWA	Ceil.	TWA	Ceil. Min.	TWA Hours			Type	Max. Load (mg)	Desorp. Eff'cy.
Acetic anhydride	102.1	1.10													
Acetone	58.1	0.79	1000		2	2	100	20	20	1.5	a	V	Charcoal	9	86±10
Acetonitrile	41.1	0.79		40									Charcoal	2.7	
Acetylene tetrabromide	345.7	2.97	1		100	100	1000	200	100	8	k	XI	Silica Gel		
Allyl alcohol	58.1	0.85	2		2	10	200	20(50)	10	8(3.3)	e	II	Charcoal	< 0.6	89±5
Allyl chloride	76.5	0.94	1		100	100	1000	200	.00	8	m	V	Charcoal		
Alpha-methyl styrene	118.2	0.91		100	2	3	200	20	10	2.5	a	II	Charcoal		
Aniline	93.1	1.02	5		6	48	200	100	30	8	c	III	Silica Gel		
Arsine	77.9		0.05		2	10	200	20(50)	10	8(3.3)	q	–	Charcoal		
Benzene	78.1	0.88	1	5	2	10	200	20(50)	10	8(3.3)	a	I	Charcoal		96
Benzyl chloride	126.6	1.10	1		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	< 0.4	90±5
Bromoform	252.8	2.9	0.5		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal		
Butadiene	54.1	GAS	1000		1	1	50	20	20	0.8	a	I	Charcoal		
2-Butanone	72.1	0.81	200		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal		
2-Butoxy ethanol	118.2	0.90	50		2	10	200	20(50)	10	8(3.3)	h	II	Charcoal		99±5
Butyl acetate	116.2	0.88	150		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal	15	99±5
Butyl alcohol	74.1	0.81	100		2	10	200	20(50)	10	8(3.3)	s	II	Charcoal	10.5	88±5
Butylamine	73.1	0.73	5		6	48	200	100	30	8	d	XIII	Silica Gel		
Camphor	152.2	0.99	2		2	10	200	20(50)	10	8(3.3)	b	II	Charcoal	13.4	98±5
Carbon tetrachloride	153.8	1.59	10	25	5	15	1000	50	5	5	a	I	Charcoal	7.5	97±5
Chlorodiphenyl (54% Chlorine)	*	*	0.5mg/m³			100		1500		1.1	i	IX	Filter		
Chlorobenzene	112.6	1.10	75		10	10	200	20(50)	50	8(3.3)	a	II	Charcoal	15.5	90±5
Chlorobromomethane	129.4	1.99	200		2	5	200	20(50)	10	4(1.5)	a	II	Charcoal	9.3	94±5
Chloroform	119.4	1.48		50	2	10	200	20(50)	10	8(3.3)	a	I	Charcoal	11	96±5
Chlorinated camphene (Toxaphene)	*	*	0.5mg/m³			15		1000		0.25	i	IX	Filter		
Cresol (All Isomers)	108.1	1.04		5										< 2.0	
Cumene	120.2	0.86	50		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	11	100
Cyclohexane	84.2	0.78	300		2	2.5	200	20	10	2	a	V	Charcoal	6.3	100
Cyclohexanol	100.2	0.96	50		2	10	200	20(50)	10	8(3.3)	e	II	Charcoal	10	99±5
Cyclohexanone	98.1	0.95	50		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	13	78±5
Cyclohexene	82.1	0.81	300		2	5	200	20(50)	10	4(1.5)	a	V	Charcoal		100
Diacetone alcohol	116.2	0.93	50		2	10	200	20(50)	10	8(3.3)	e	II	Charcoal	12	77±10
Diazomethane	42.0	GAS	0.2			10		200		0.8	a	XII	Coated R.		
Dibutyl phthalate	278.3	1.04	5mg/m³			30		1000		0.5	a	VIII	Filter		
1,1-Dichloroethane	99.0	1.18	100		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	7.5	100
1,2-Dichloroethylene	97.0	1.28	200		2	3	200	20(50)	10	2.5(1.0)	a	II	Charcoal	5.1	100
Diethylamine	73.1	0.71	25		50	50	1000	100	50	8	r	XIII	Silica Gel		
Di-2-ethylhexyl phthalate	390.6	0.99	5mg/m³			30		1000		0.5	a	VIII	Filter		
Difluorodibromomethane	209.8		100		2	10	200	20(50)	10	8(3.3)	n	II	Charcoal		
Diisopropylamine	101.2	0.72	5		6	48	200	100	30	8	d	XIII	Silica Gel		
Dimethylamine	45.1	0.68	10		50	50	1000	100	50	8	r	XIII	Silica Gel		
Dioxane	88.1	1.03	100		2	10	200	20(50)	10	8(3.3)	a	I	Charcoal	13	91±5
Dimethyl analine	122.2	0.96													
Dipropylene glycol methyl ether	148.2	0.95	100		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal		75±15
Epichlorohydrin	92.5	1.18	5		20	20	200	50	100	8	a	II	Charcoal		
2-Ethoxyethyl acetate	132.2	0.98	100		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal	19	74±10
Ethyl acetate	88.1	0.90	400		2	6	200	20(50)	10	5(2)	a	VII	Charcoal	12.5	89±5
Ethyl acrylate	100.1	0.94	25		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal		95±5
Ethyl alcohol	46.1	0.80	1000					50	20	0.33	f	II	Charcoal	2.6	77±10
Ethylamine	45.1	0.69	10		6	48	200	100	30	8	d	XIII	Silica Gel		
Ethyl benzene	106.2	0.87	100		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	16	100
Ethyl bromide	109.0	1.45	200		2	4	200	20(50)	10	3.3(1.3)	n	II	Charcoal	7.1	83±5
Ethyl butyl ketone	114.2	0.82	50		2	10	200	20(50)	10	8(3.3)	b	II	Charcoal	< 5.5	93±5
Ethylene chlorohydrin	80.5	1.20	5		2	10	200	20(50)	10	8(3.3)	e	II	Charcoal	16	92±5
Ethylene dibromide	187.9	2.17	20	30	2	10	200	200	10	0.8	a	II	Charcoal	< 10.7	93±5
Ethylene dichloride	99.0	1.26	50	100	3	10	200	20(50)	15	8(3.3)	a	XV	Charcoal	12	95±5
Ethyl ether	74.1	0.73	400		2	3	200	20(50)	10	2.5(1)	j	V	Charcoal	7.5	98±5
Ethyl formate	74.1	0.92	100		2	10	200	20(50)	10	8(3.3)	a	I	Charcoal	4.8	80±10
Glycidol	74.1	1.11	50		2	10	200	20(50)	10	8(3.3)	k	II	Charcoal		
Heptane	100.2	0.68	500		2	4	200	20(50)	10	3.3(1.3)	a	XV	Charcoal	12.5	96±5
Hexachloronaphthalene	*	*	0.2mg/m³			30		1000		0.5	i	VIII	Filter		
Hexane	86.2	0.66	500		2	4	200	20(50)	10	3.3(1.3)	a	I	Charcoal	11	94±5
Hexone (MEK)	100.2	0.80	100		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal		
Isoamyl acetate	130.2	0.88	100		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal	16.5	90±5
Isoamyl alcohol	88.2	0.81	100		2	10	200	20(50)	10	8(3.3)	e	II	Charcoal	10	99±5
Isobutyl acetate	116.2	0.87	150		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal	14	92±5
Isobutyl alcohol	74.1	0.81	100		2	10	200	20(50)	10	8(3.3)	s	II	Charcoal	10.5	84±10
Isopropyl acetate	102.1	0.87	250		2	9	200	20(50)	10	7(3)	a	VII	Charcoal	13	85±5
Isopropyl alcohol	60.1	0.79	400		2	3	200	20(50)	10	2.5(1)	f	II	Charcoal	5.6	94±5
Isoproplyamine	59.1	0.69	5		6	48	200	100	30	8	d	XIII	Silica Gel		

Continued

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TABLE A4-3. (Continued)

Chemical With Established Procedure	* Molecular Weight (g/mole)	* Density (g/ml)	OSHA Standard		Sample Volume Liters		Sample Rate ml/min.		Sample Time		Desorp. Sol. (Eluent)	GC Column	Sample Tubes		
			TWA ppm	Ceil. ppm	Ceil.	TWA	Ceil.	TWA	Ceil. Min.	TWA Hours			Type	Max. Load (mg)	Desorp. Eff'cy.
Isopropyl glycidyl ether	116.2		50		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	10.5	80±10
Ketene	42.0	GAS	0.9mg/m³			50		1000		0.8			Impinger		
Mercury	200.6	13.59	0.1mg/m³		10		1000		10				Charcoal		
Mesityl oxide	98.1	0.86	25		2	10	200	20(50)		8(3.3)	b	II	Charcoal	4.8	79±5
Methyl acetate	74.1	0.93	200		2	7	200	20(50)	10	5.5(2.3)	a	I	Charcoal	7	88±5
Methyl acrylate	86.1	0.96	10		2	5	200	20(50)	10	4(1.5)	a	VII	Charcoal	~15	80±10
Methyl alcohol	32.0	0.79	200		2	5	200	20(50)	10	4(1.5)	g	II	Silica Gel		
Methylal (dimethoxymethane)			1000		2	2	200	20(50)	10	1.5(0.6)	i	V	Charcoal		
Methylamine	31.1	GAS	10		6	68	200	100	30	8	d	XIII	Silica Gel		
Methyl cellosolve	76.1	0.97	25		2	10	200	20(50)	10	8(3.3)	h	II	Charcoal	10	97±5
Methyl cellosolve acetate	118.1	1.0	25		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal	5	76±10
Methyl chloroform	133.4	1.35	350		2	6	200	20(50)	10	5(2)	a	XV	Charcoal	18	98±
Methyl cyclohexane	98.2	0.77	500		2	4	200	20(50)	10	3.3(1.3)	a	I	Charcoal		95±5
Methylene chloride	84.9	1.33	500	1000	1	2.2	200	20(50)	5	1.8(0.7)	a	I	Charcoal	9.3	95±5
Methyl ethyl ketone (See 2-Butanone)	72.1	0.81													
5-Methyl-3-heptanone	128.2	0.82	25		2	10	200	20(50)	10	8(3.3)	b	II	Charcoal		
Methyl iodide	142.0	2.28	5		2	10	200	20(50)	10	8(3.3)	e	XV	Charcoal		
Methyl-iso-amyl-acetate	144.2	0.86	50		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal		
Methyl isobutyl carbinol	102.2	0.80	25		2	10	200	20(50)	10	8(3.3)	e	II	Charcoal		
Methyl-n-amyl-ketone	114.2	0.82	100		2	10	200	20(50)	10	8(3.3)	b	II	Charcoal		
n-amyl acetate	130.2	0.88	100		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal		
Naptha, coal tar	*	*	100		2	10	200	20(50)	10	8(3.3)	a	XVI	Charcoal	16.8	88±5
n-butyl glycidyl ether	130.2		50		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal		
N,N dimethylaniline	121.2	0.96													
n-propyl acetate	102.1	0.84	200		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal		
O-anisidine	123.2	1.10	0.1		240	480	1000	1000	4 hrs.	8	c	III	Silica Gel		
Octachloronaphthalene	403.7	–	0.1mg/m³			30		1000		0.5	1	VIII	Filter		
Octane	114.2	0.70	500		2	4	200	20(50)	10	3.3(1.3)	a	I	Charcoal	15	93±5
O-dichlorobenzene	147.0	1.31		50	3	3	200	20	15	2.5	a	XV	Charcoal		
O-toluidine	107.2	1.01													
P-anisidine	123.2	1.09	0.1		240	480	1000	1000	4 hrs.	8	c	III	Silica Gel		
Pentane	72.2	0.63	1000		2	2	50	20	40	1.5	a	I	Charcoal	9	95±5
2-Pentanone	86.1	0.81	200		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal		88±5
Petroleum distillate	*	*	500		2	4	200	20(50)	10	3.3(1.3)	a	XV	Charcoal	12.3	96±5
Phenol	94.1	1.07		5											
Phenyl ether (vapor)	170.2	1.10	1		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	0.6	90±5
Phenyl ether-biphenyl	170.2	1.10	1		2	10	200	20(50)	10	8(3.3)	m	X	Silica Gel		
Phenyl glycidyl ether	150.2		10		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	12.5	97±5
Phenyl hydrazine	108.1	1.10													
P-nitroaniline	138.1	0.90	1		90	96	1000	200	90	8	c	III	Silica Gel		
Propyl alcohol	60.1	0.72	200		2	10	200	20(50)	10	8(3.3)	c	II	Charcoal	9	87±5
Propylene dichloride	113.0	1.16	75		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	3	97±5
Propylene oxide	58.1	0.83	100		2	5	200	20(50)	10	4(1.5)	a	V	Charcoal	3	90±5
P-tert-butyltoluene	148.2	0.85	10		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal		
Pyridine	79.1	0.98		5								XIII		~7.3	70±10
Sec-amyl acetate	130.2	0.88	125		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal		
Sec-butyl acetate	116.2	0.89	200		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal		
Sec-butyl alcohol	74.1	0.81	150		2	10	200	20(50)	10	8(3.3)	s	II	Charcoal		
Stoddard solvent	*	*	500		2	3	200	20(50)	10	2.5(1)	a	XVI	Charcoal	13	96±5
Styrene	104.1	0.91	100	200	2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	18	87±5
Terphenyls (ortho-terphenyl)	230.3			1	15		1000		15		a	VI	Filter		
Tert-butyl acetate	116.2	0.87	200		2	10	200	20(50)	10	8(3.3)	a	VII	Charcoal		
Tert-butyl alcohol	74.1	0.79	100		2	10	200	20(50)	10	8(3.3)	f	II	Charcoal		
1,1,2,2-Tetrachloro-1,2-difluoroethane	203.8	1.64	500		2	2	50	20	40	1.6	a	II	Charcoal		
1,1,1,2-Tetrachloro-2,2-difluoroethane	203.8	GAS	500		2	2	35	20	55	1.6	a	II	Charcoal	19.5	100
1,1,2,2-Tetrachloroethane	167.9	1.59	5		10	10	200	20(50)	50	8(3.3)	a	II	Charcoal	6.5	85±5
Tetrachloroethylene	165.9	1.63	100	200	3	10	200	20(50)	15	8(3.3)	a	XV	Charcoal		
Tetrahydrofuran	72.1	0.89	200		2	9	200	20(50)	10	7(3)	a	V	Charcoal	7.5	92±5
Toluene	92.1	0.87	200	300	2	10	200	20(50)	10	8(3.3)	a	I	Charcoal		92±5
1,1,2-Trichloro-1,2,2-trifluoroethane	187.4	1.56	1000		1.5	1.5	50	20	30	1.25	a	XIV	Charcoal		
1,1,2-Trichloroethane	133.4	1.44	10		2	10	200	20(50)	10	8(3.3)	a	XV	Charcoal	5	96±5
Trichloroethylene	131.4	1.47	100	200	3	10	200	20(50)	15	8(3.3)	a	XV	Charcoal	21	96±5
1,2,3-Trichloropropane	147.4	1.39	50		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal		
Triethylamine	101.2	0.73	25		6	68	200	100	30	8	d	XIII	Silica Gel		
Trifluoromonobromomethane	148.9	GAS	1000		1	1	50	20	20	0.8	p	V	Charcoal	25	
Turpentine	256.0	0.87	100		2	10	200	20(50)	10	8(3.3)	a	XVI	Charcoal	13	56±5
Vinyl chloride	62.5	GAS		1							a	I	Charcoal		
Vinyl toluene	118.1	0.89	100		2	10	200	20(50)	10	8(3.3)	a	II	Charcoal	17	85±10
Xylene	106.2	0.86	100	150	2	10	200	20(50)	10	8(3.3)	a	I	Charcoal		95±5
2-4-Xylidine	121.2	0.98													

multicomponent atmospheres, and (5) unproven applicability of this method to compounds not listed in Table A4-3.

Using GC/MS to quantitate on a desirable 50 ng/specie-of-interest basis, 450 ppb is an attainable detection limit for an organic compound with a molecular weight of 120 with a 10 liter breakthrough volume.

4.2.1.3 XAD-2 Adsorbent Systems

For the collection of relatively nonvolatile compounds present in the gaseous phase, XAD-2 can be used. The collected compounds from the XAD-2 are removed by Soxhlet extraction with ether, concentrated and quantified by GC/MS.

The resin module was designed using the Arthur D. Little sorbent evaluation data.[11] The ADL data is for low challenge concentrations (< 100 ppm total hydrocarbons to the resin) with volatile (BP 120°C) organics.

The advantages of XAD-2 are high adsorption efficiencies, effective desorption of polar and high boiling compounds, low cost and shorter sampling time compared to charcoal tube sampling using a NIOSH protocol. The disadvantages of using XAD-2 are that (1) nonpolar compounds boiling below approximately 140°C may not be retained on the resin, (2) compounds boiling below approximately 100°C can be lost in the extraction and concentration steps, and (3) XAD-2 adsorbent often exhibits a high background (alkyl benzenes, naphthalenes) which interferes with the quantification of compounds in that range. The cleanup procedure to reduce the background is time consuming (approximately one week) and if the resin is broken, more unwashed surfaces are exposed to contribute to the background. Breakthrough volumes for the higher boiling compounds trapped by XAD-2 have not been reported as part of the ADL sorbent evaluation. However, the breakthrough volume appears to be 10^3 ℓ/g of XAD-2. The sampling module used was designed for 5 ℓ/min flow and 10 ℓ/min is recommended as a maximum flow rate. This is equivalent to 600 liters of air containing 15 ppb of a material having a molecular weight of 150.

In all of the detection limits approximations, the concentrations are stated as ppb to the sorbent trap.

The utilization of Amberlite XAD-2 resin for sampling of trace organics in gases requires a rigorous precleaning procedure to minimize contamination. Radian has developed a procedure for preparing XAD-2 resin for gaseous sampling.

The resin preparation procedure accomplishes three basic goals:

- removal of inorganic salts,
- removal of organic contaminants, and
- storage of resin in a suitable state for sampling.

The procedure is described in the following steps:

A. The resin as received contains fines and inorganic salts. Removal of these substances is accomplished by washing the resin with water until the water is clear.

B. The wet resin is extracted with methanol in a Soxhlet type extractor for twenty-four hours. This step serves both to remove the remaining water and inorganic salts and to perform an initial removal of organics.

C. The resin is then extracted for twenty-four hours with pyridine in a Soxhlet extractor. This is followed by a twenty-four hour extraction with diethyl ether. These extractions remove the remaining organic contaminants.

D. The resin is then removed from the extractor and washed with methanol. After washing, the resin is transferred to a glass container and stored under methanol.

The major source of contamination in the resin is rupturing of the beads after clean-up, releasing organics from the beads. The procedure described above minimizes this problem by never allowing the resin to dry or be exposed to excessive heat and by maintaining a degree of hydration in the resin by storing under methanol.

Immediately prior to sampling, the resin is transferred to the resin container, the methanol drained off, and the resin rinsed with a small amount of organic free water. Sampling is then performed on the wet resin which may be returned to the laboratory in this fashion for subsequent analysis.

4.2.2 Collection of Samples

4.2.2.1 Fugitive Emissions

Collection of Leaking Vapor for Species Identification--Samples of the leaking vapor were collected on Tenax adsorbent, XAD-2 resin, and charcoal. The air containing hydrocarbons from the enclosed leaking valve was passed through tubes containing the various adsorbents. Both the "draw-through" and the "blow-through" methods were used for this purpose.

The nominal operating conditions for the various adsorbents are presented in Table A4-4. Before sampling was started, the hydrocarbon content of the air was determined by GC. The hydrocarbon loadings on the various adsorbents were calculated from the sampling time, air flow rate through the adsorbent, and hydrocarbon content of the air.

The "Blow-Through" Method--Schematic diagrams of the sampling train used with the "blow-through" method of measuring hydrocarbon emission rates are shown in Figures A4-2a and A4-2b.

In this method, plant air is used as the source of diluent air to the enclosure around the leaking source. Plant air is first passed through an activated carbon canister to remove contaminants. The air then passes through a dry gas meter and into the enclosure. The air is exhausted from the enclosure through a line connected to the opposite side of the tent. A fraction of the exit air is continually drawn through an air driven vacuum (sampling) pump. When equilibrium has been established, this fraction of the air stream is collected

TABLE A4-4. NOMINAL OPERATING CONDITIONS FOR SAMPLING WITH ADSORBENTS

			Recommended Ranges			
Sorbent	Detection Limit	Method	Volume	Flow	Mass	Inlet Concentration
TENAX	~ 1 ppb	GC/MS	1 - 2 ℓ	10 - 25 ml/min	50 - 100 ng minimum	5 - 20 ppbv
Charcoal	~ 500 ppb	GC/MS	5 - 10 ℓ	20 - 50 ml/min	2 - 15 mg	200 - 500 ppmv
	~ 50 ppm	GC				
XAD-2	~ 50 - 100 ppb	GC/MS	300 -600 ℓ	5 - 10 1/min	3 - 4 g maximum	100 - 1000 ppmv

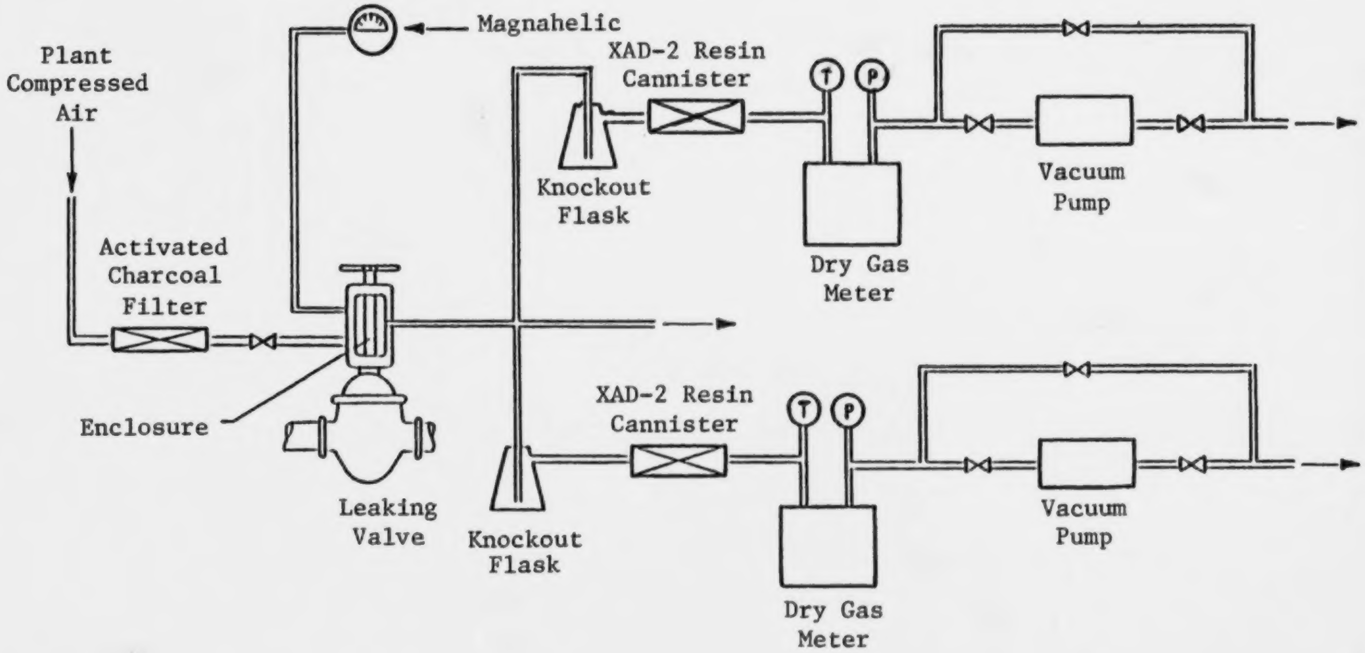

Plant Compressed Air
Magnahelic
Activated Charcoal Filter
Enclosure
Leaking Valve
Knockout Flask
XAD-2 Resin Cannister
T
P
Dry Gas Meter
Vacuum Pump
XAD-2 Resin Cannister
Knockout Flask
T
P
Dry Gas Meter
Vacuum Pump

Figure A4-2a. Typical Sampling Train for Taking Gas Samples on XAD-2 Resin Using the Blow-Through Method.

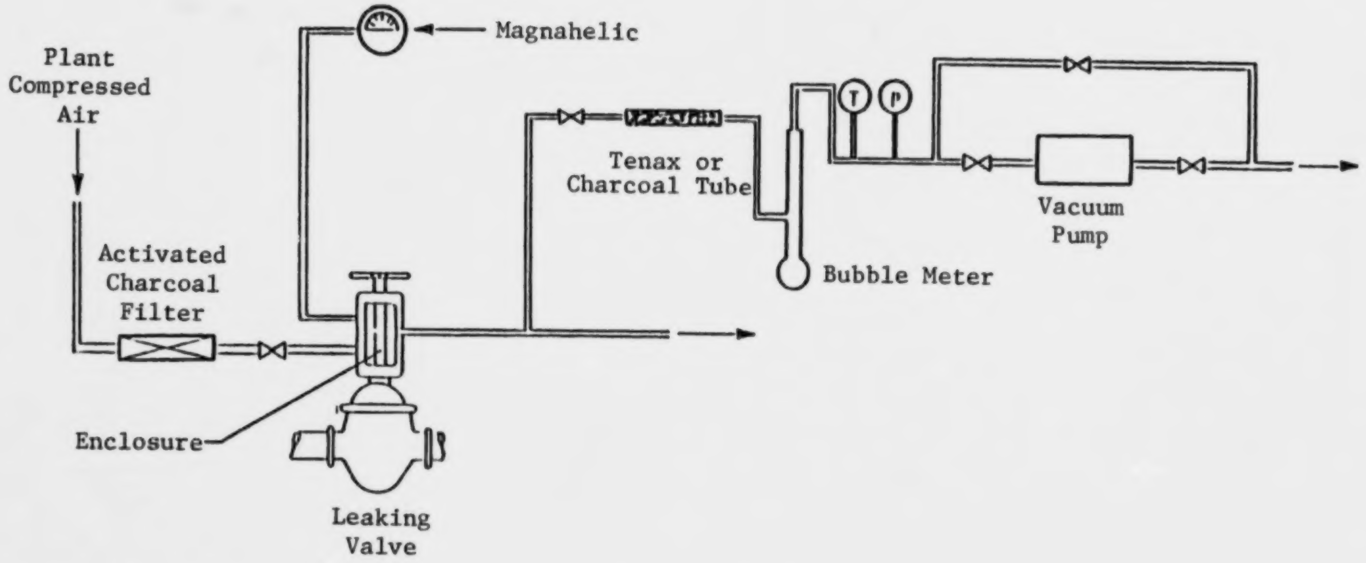

Plant Compressed Air
Magnahelic
Activated Charcoal Filter
Enclosure
Leaking Valve
Tenax or Charcoal Tube
T
P
Bubble Meter
Vacuum Pump

Figure A4-2b. Typical Sampling Train for Taking Gas Samples on Tenax Resin and Charcoal Using Blow-Through Method.

in a plastic bag. The contents are then analyzed for methane and total nonmethane hydrocarbon using gas chromatographs equipped with flame ionization detectors.

The hydrocarbon emission rates can be calculated from the inlet air flow rate and the hydrocarbon concentration in the outlet air. The "blow-through" method can be used when very low or very high flow rates of air are required.

Collection of Samples Using the "Blow-Through" Method-- A schematic diagram of the sampling train used to collect vapor samples on various adsorbents by the "blow-through" method is shown in Figures A4-2. The XAD-2 resin canisters are large and contain ~ 100 gm of adsorbent. A substantial amount of air had to be passed through a canister to provide enough adsorbent hydrocarbon for accurate analysis. It was necessary in most cases, to operate the sampling train for one to two hours for an adequate XAD-2 resin sample.

Two sample lines were connected to the enclosure outlet line. Air was drawn through each line with an air-driven vacuum pump. The flow rate was adjusted to conform to the operating conditions shown in Table A4-4. The hydrocarbon concentration of the air was measured by taking air samples in plastic bags and analyzing the contents by GC to determine nonmethane hydrocarbon content.

The air flow out the end of the enclosure outlet line was monitored to insure that a positive flow of air was maintained at all times.

A similar system was used to obtain charcoal and Tenax resin samples. A schematic flow diagram of the system is shown in Figure A4-2b. Samples of each type were normally taken. However, the hydrocarbon loading on the charcoal and Tenax was much lower than that on the XAD adsorbent. The individual sampling time was normally 5 to 20 minutes. The sample air was pulled through the Tenax or charcoal tube with an air-driven vacuum pump. The required air flow rates were quite low (see Table A4-4), and a bubble meter was used to set and measure these rates. The total hydrocarbon adsorbed on the adsorbent was calculated from the air flow rate through the tubes, the sampling time, and the hydrocarbon content of the air.

The "Flow-Through" Method--Schematic diagrams of the sampling train assembled for "flow-through" sampling are shown in Figures A4-3a and A4-3b. A Mylar plastic enclosure was made around the suspected leak. The size of this enclosure was kept as small as practical.

A continuous flow of air was established by the air-driven vacuum pump and metered by means of the dry gas meter and a stopwatch. The temperature and pressure at the meter were recorded to convert the flow rate to standard conditions. Once equilibrium was established, a gas sample was withdrawn by a small sample pump, transferred to a plastic bag and analyzed for methane and nonmethane hydrocarbon. The hydrocarbon emission rate was calculated from the air flow rate and the hydrocarbon concentrations.

Collection of Samples Using the "Flow-Through" Method--The "flow-through" method for taking vapor samples on adsorbents differs from the "blow-through" method in only one way. Instead of blowing air through the enclosure around the

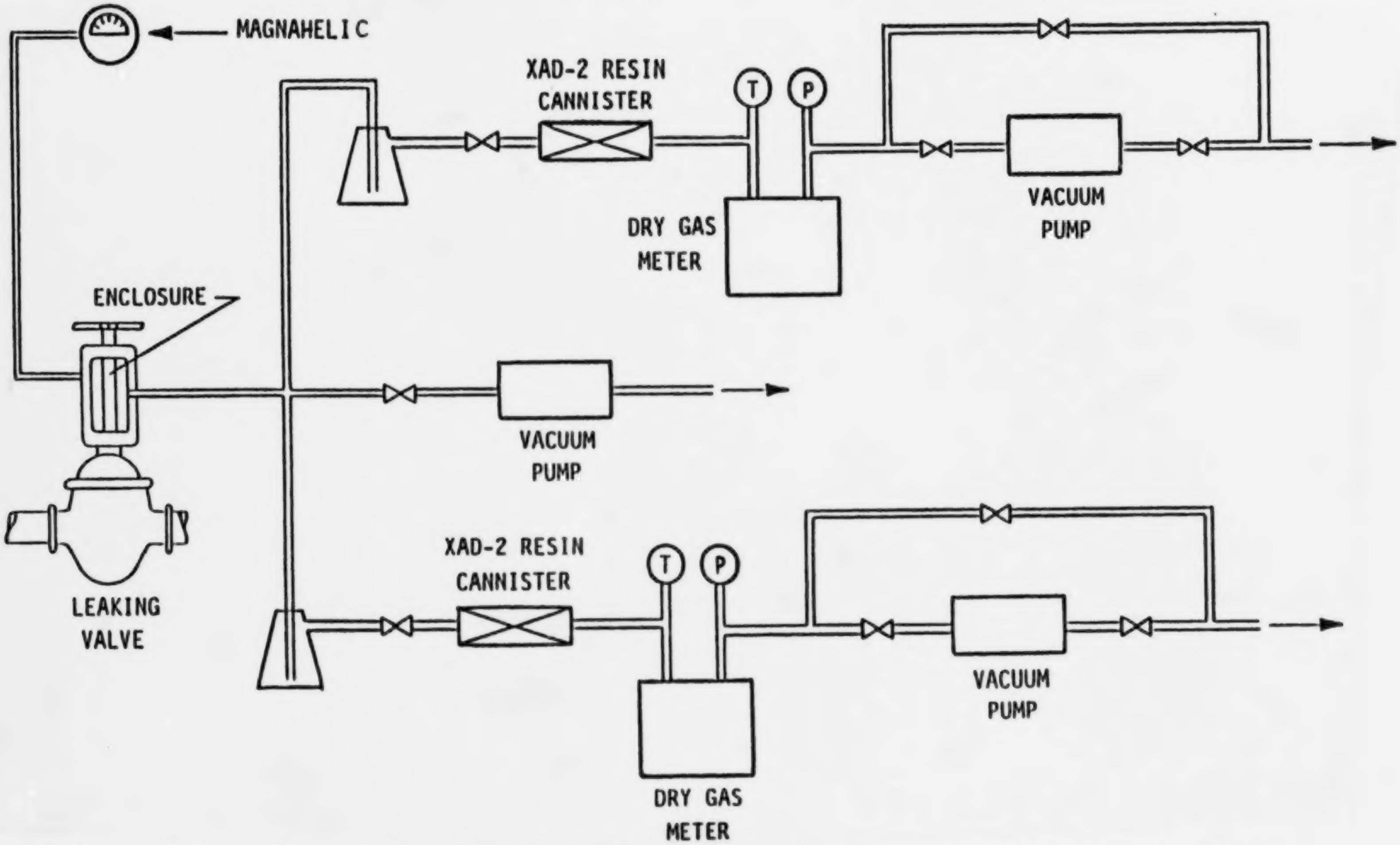

MAGNAHELIC
XAD-2 RESIN CANNISTER
T
P
DRY GAS METER
VACUUM PUMP
ENCLOSURE
VACUUM PUMP
LEAKING VALVE
XAD-2 RESIN CANNISTER
T
P
DRY GAS METER
VACUUM PUMP

Figure A4-3a. Typical Sampling Train for Taking Gas Samples on XAD-2 Resin Using the Flow-Through Method.

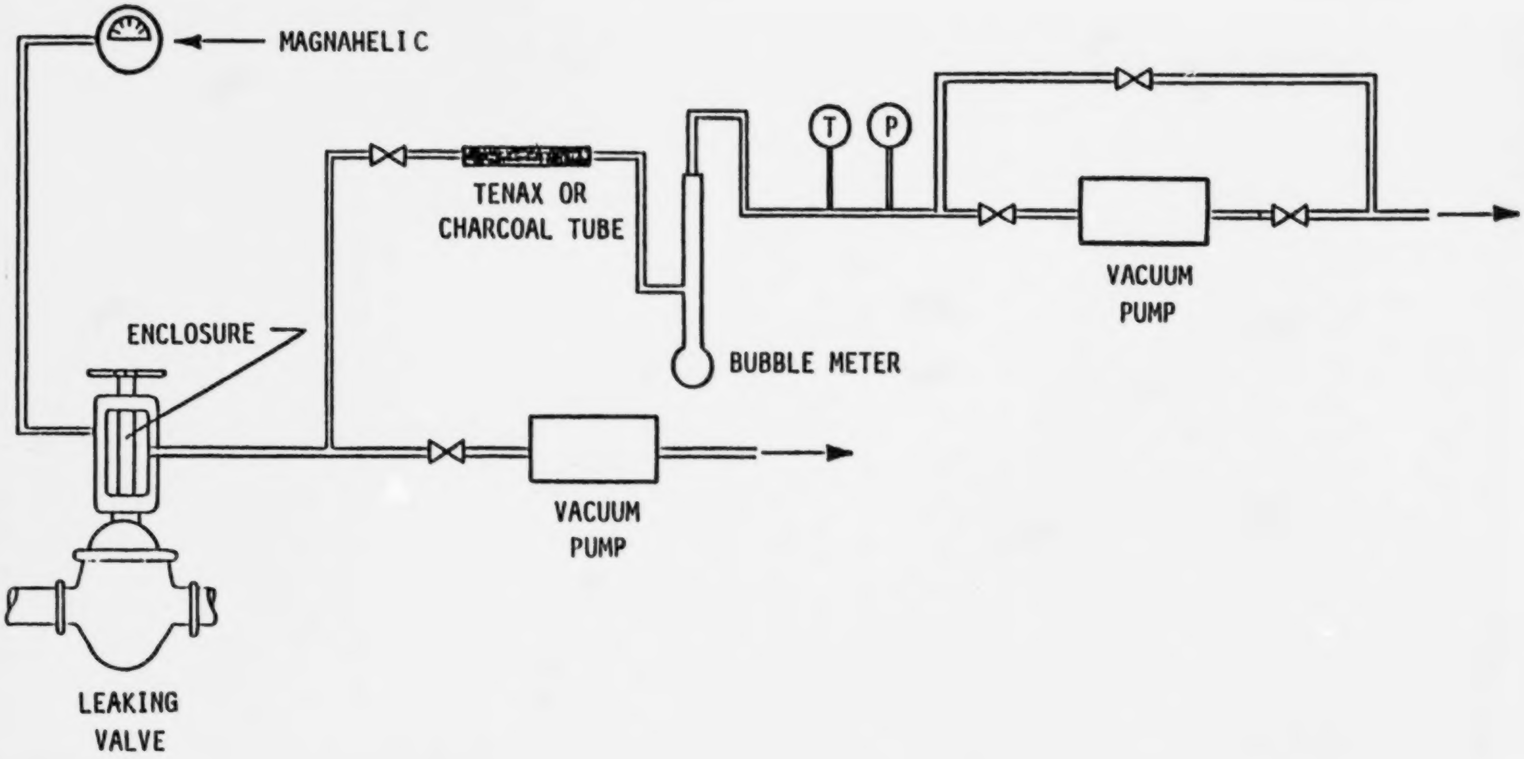

MAGNAHELIC
TENAX OR CHARCOAL TUBE
T
P
ENCLOSURE
BUBBLE METER
VACUUM PUMP
VACUUM PUMP
LEAKING VALVE

Figure A4-3b. Typical Sampling Train for Taking Gas Samples on Tenax Resin and Charcoal Using the Flow-Through Method.

leaking source, ambient air is drawn into and through the enclosure with a vacuum pump.

The schematic diagrams of the XAD-2 and the Tenax resin/charcoal sampling systems are shown in Figures A4-3a and A4-3b.

Collection of Bulk Liquid Samples--Samples of various representative liquid streams were collected from sampling points along the processing lines. All samples were taken in Pyrex sample bottles, tightly sealed with Teflon-lined screw caps, and refrigerated until analyzed.

4.2.2.2 Flue Gas and Particulate Sampling

Samples for trace organics speciation were collected from the selected stack using a modified Aerotherm Source Assessment Sampling System (SASS). (See Figure A4-4 and Figure A4-5.) A 1154 SCF sample of stack gas was drawn from a point of average velocity in the stack. The particulates were removed on a filter, and the gas was then cooled and passed through a sorbent canister filled with XAD-2 resin to trap any nonvolatile organic compounds. The particulates, the condensate that resulted from cooling the gas, and the XAD-2 resin were collected and returned to Austin for extraction and analysis.

The organic concentrator for the SASS train is a canister filled with XAD-2 resin. It replaces the canister that comes with the SASS train.

Treating Canister Resin--The XAD-2 resin was left in the methanol solution until ready for treatment. At least six

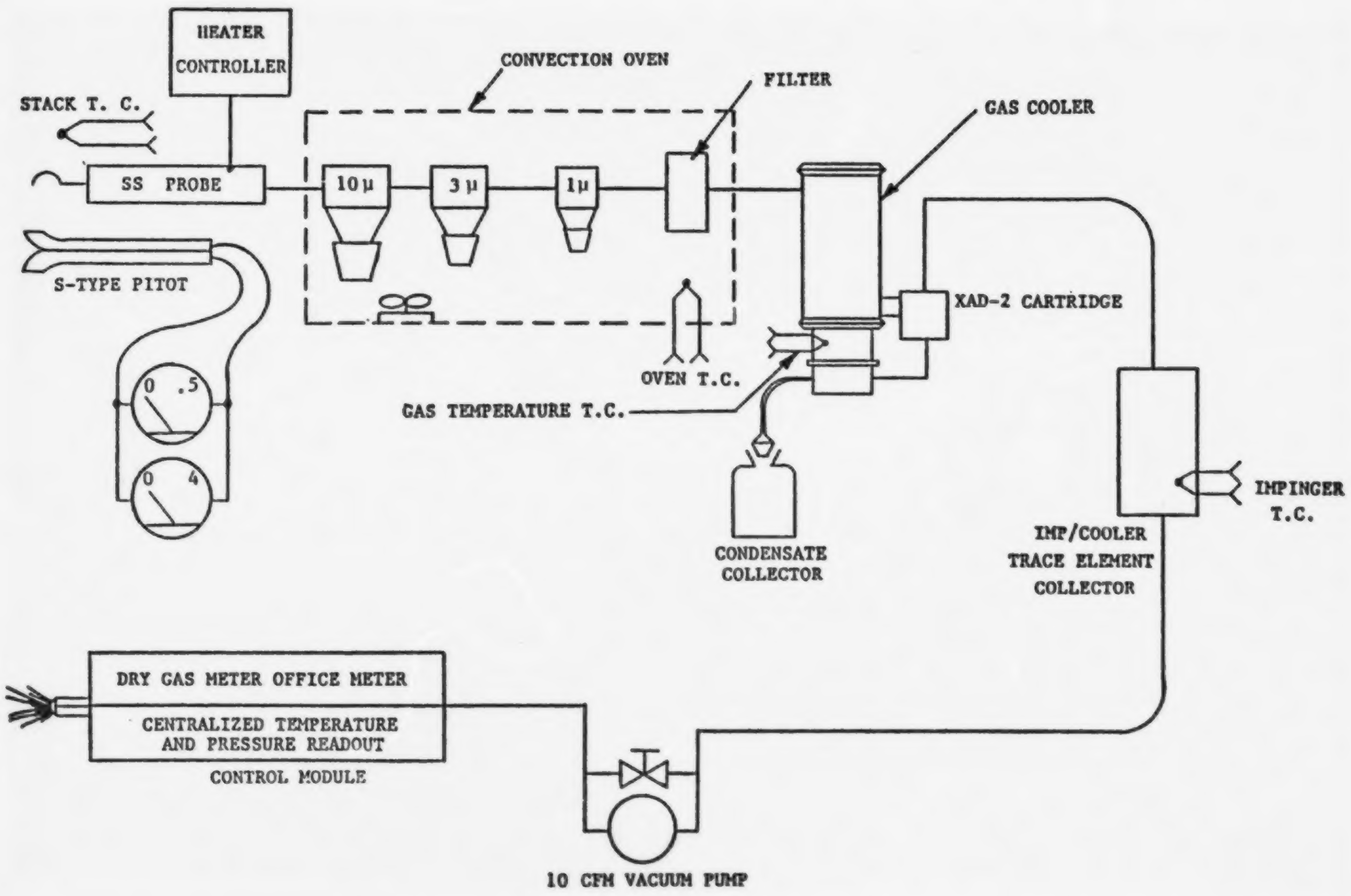

HEATER CONTROLLER
CONVECTION OVEN
FILTER
GAS COOLER
STACK T. C.
SS PROBE
10μ
3μ
1μ
S-TYPE PITOT
0 .5
0 4
XAD-2 CARTRIDGE
OVEN T.C.
GAS TEMPERATURE T.C.
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER OFFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMP

Figure A4-4. Source Assessment Sampling System

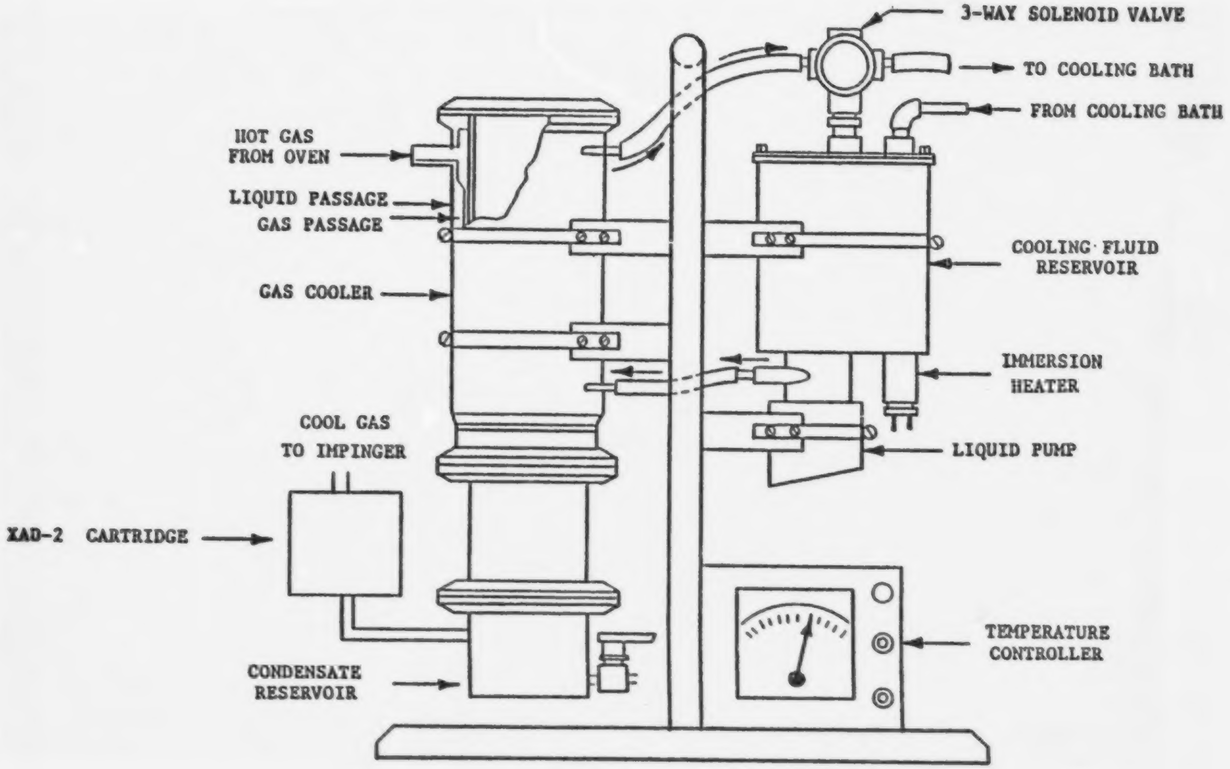

3-WAY SOLENOID VALVE
TO COOLING BATH
FROM COOLING BATH
HOT GAS FROM OVEN
LIQUID PASSAGE
GAS PASSAGE
COOLING FLUID RESERVOIR
GAS COOLER
IMMERSION HEATER
COOL GAS TO IMPINGER
LIQUID PUMP
XAD-2 CARTRIDGE
TEMPERATURE CONTROLLER
CONDENSATE RESERVOIR

Figure A4-5. XAD-2 Sorbent Trap Module

hours before sampling but not more than twenty-four hours, the caps were removed from the canister and all the methanol was drained off. The canister resin (through the end-cap fittings) was rinsed with ~ 1500 ml of organic free water. A dry nitrogen gas source was fastened to the canister. A flow rate was controlled between 100 ml to 200 ml per minute.

The canister was heated to 60°C but not more than 100°C to drive off the water. This took approximately four hours. A mirror was used to test for moisture coming from the open end of the heated canister. When all water was removed, the nitrogen flow was stopped and the canister was capped. The organic concentrator was then ready to be used for sampling.

Attaching Canister to SASS Train--The original equipment organic concentrator was removed from the SASS train; therefore, the canister was coupled directly to the water trap reservoir.

Cleaning the Canister--The canister was taken out of the train and flushed briefly with nitrogen. Both ends were capped. All fittings other than the canister were rinsed as described in the Level One procedure[12] and the organic solvents were saved.

4.2.3 Transportation and Storage

At the end of the sampling process, the charcoal and resin tubes were removed from the sampling system, sealed at both ends, and placed in a freezer in the mobile laboratory. They were kept frozen until the sample tubes were processed for analysis. The liquid samples were sealed in glass bottles and refrigerated until analyses were performed.

When all the speciation samples were obtained, they were sent back to the Radian laboratory in Austin for analysis on the GC/MS. They were shipped by air freight or hand carried to Austin where they were stored in freezers or refrigerators.

5.0 FIELD ANALYSES

5.1 Mobile Laboratory

Radian had a mobile laboratory dedicated to the fugitive emission sampling in refineries. This laboratory is described below.

The laboratory is housed in an 8' × 26' van trailer and has the capability of supporting a wide variety of sampling and analytical procedures. The forward area is equipped with counter space and utilities to support the wide variety of analytical instruments contained in the trailer.

The remainder of the laboratory is equipped with standard wet-chemistry benches and extensive equipment storage space. A fume hood, with externally mounted explosion-proof blowers, has been provided for containment of hazardous experiments and exhaust of vapors. Electrical, water, and drainage utilities needed to operate the laboratory are obtained on-site, and external connections are provided to interface with the required services. Electric service required is 100 amps at 220 volts single-phase supplied to a junction box equipped to connect to a 3 wire No. 2 pigtail. Water service can be supplied by standard high-pressure, three-quarter inch water hose. The drainage system is adaptable to site requirements. All external components of the air-conditioning system are explosion proof.

This trailer was specially equipped for the refinery sampling program. It contained the primary instrumentation items:

- Hewlett-Packard 5730A gas chromatograph with duel FID and flame photometric detectors,

- Hewlett-Packard 3380 reporting integrator,

- Dohrmann DC 53D Total Organic Carbon Analyzer,

- Byron Model 301C Total Hydrocarbon Analyzer specially built for Radian,

- Monitor Labs chemiluminescent NO/NO_x analyzer and support equipment,

- Wilks Miran 1A portable infrared analyzer with 21-meter variable path-length gas cell,

- Fisher Gas Partitioner Model 1200 gas chromatograph,

- Bausch and Lomb Spectronic 21 UV-Vis spectrophotometer,

- 2 Mettler balances, analytical and top-loading,

- Tracor Model 432 Triperm Permeation tube calibration system,

- complete complement of glassware and facilities for wet chemistry,

- Aerotherm Source Assessment Sampling Train equipped for high-rate sampling, particulate size cuts and vapor collections,

- Radian-made aldehyde sampling train,

- Lear Siegler PM 100 Manual Stack Sampler for EPA Method 5,

- heated and dehumidified grab sampler with probe,

- two fugitive emission sampling trains with electric/air-driven pump motors, dry gas meters, sensitive manometers, sample take-off valves and cold traps, and

- Bacharach TLV hydrocarbon sniffers.

5.2 Total Hydrocarbon Content (Methane/Nonmethane)

The analysis for methane and nonmethane hydrocarbon content of fugitive emission gas samples was accomplished using a specially designed Total Hydrocarbon Analyzer (THC) Model 301C made for Radian by Byron Instruments. The instrument is made to accept samples by:

- sampling from a bag,
- syringe injection, and
- unattended, continuous in-line sampling.

Analysis of baggable samples of gas was accomplished by pumping gas out of the Mylar sampling bag into a gas sample loop using an integral pump in the THC analyzer. The instrument operates automatically after being connected to the bag. The results of the first run were discarded to avoid contamination occurring from sample retained from the previous analysis or ambient air entering the system during sample changing. Two additional runs are made and the results recorded by a strip-chart recorder.

The instrument has several ranges for both methane and nonmethane hydrocarbons. The full-scale direct readout ranges are from 0 - 2 to 0 - 20,000 ppm by weight. When these ranges were exceeded, a portion of the sample was diluted with zero grade air until it could be analyzed on one of the above ranges. Then the dilution factor was used to calculate the original concentration.

The THC uses a flame ionization detector for measurement of hydrocarbon concentration and, thus, produces a linear readout over the entire range of the instrument. Hydrocarbon-free air is used for the carrier gas.

5.2.1 Theory of Operation of a Flame Ionization Detector (FID)

When most organic compounds are burned in a hydrogen-air flame, charged particles or ions are produced. Positive and negative ions plus free electrons are produced when the sample passes through the flame. A pair of electrodes with a polarizing voltage applied collects these ions and the resulting current is amplified by an electrometer.

The flame ionization detector is actually an extremely simple device. All of the essential features are shown in the figure below.

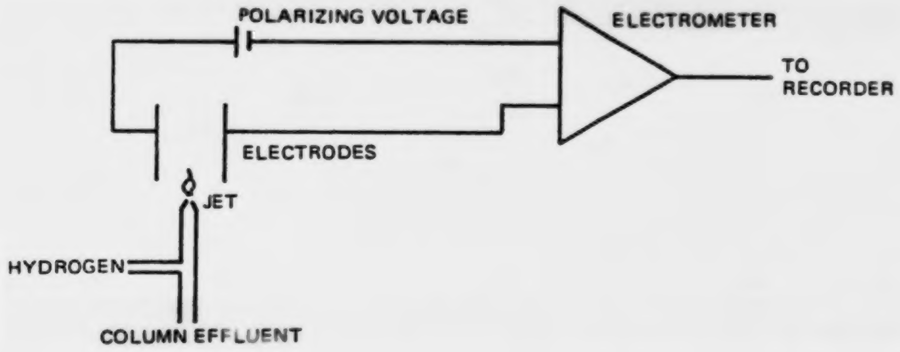

POLARIZING VOLTAGE
ELECTROMETER
TO RECORDER
ELECTRODES
JET
HYDROGEN
COLUMN EFFLUENT

Figure A5-1. Flame Ionization Detector

The sample stream is fed to the flame by mixing the column effluent with the hydrogen supply, and a separate air stream (not shown) is used to support combustion.

The response (voltage output) varies with the nature of the compound. The signal on a molar basis is roughly proportional to the number of carbon atoms in the compound.

The response from an FID is proportional to the weight of solute passing in unit time through the burner and this is true for hydrocarbons over six orders of magnitude of concentrations. (See Figure A5-2.)

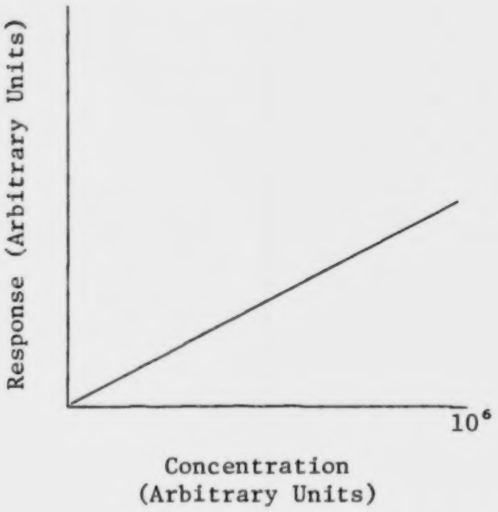


Figure A5-2. Area Response Versus Concentration

If one plots response versus molar concentration (moles/ℓ, ppmv, etc.) a family of curves is generated. For a given response from the detector one must know the identity of the hydrocarbon in order to find the true concentration of that specific compound. (See Figure A5-3.)

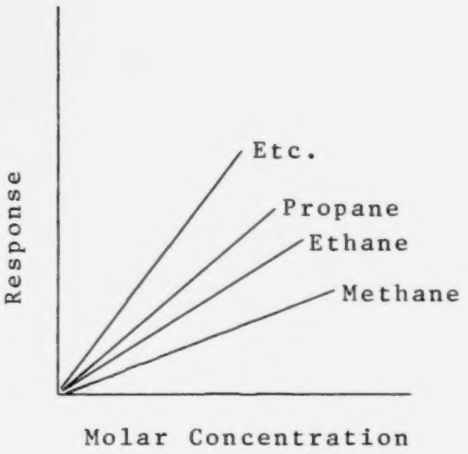


Figure A5-3. Area Response Versus Molar Concentration

What do weight response factors look like? Table A5-1 shows the relative response factors (relative sensitivities) when equal weights of material are introduced into the FID. A plot of response versus weight concentration (i.e., weight %, g/ℓ, ppmW, etc.) generates the same line within a few percent. Consequently, the specific identity of the hydrocarbon need not be known. (See Figure A5-4.)

TABLE A5-1. FID RELATIVE SENSITIVITIES

Compound	Relative Sensitivity	Compound	Relative Sensitivity
Normal Parraffins		Aromatics	
Methane	0.97	Benzene	1.12
Ethane	0.97	Toluene	1.07
Propane	0.98	Ethylbenzene	1.03
Butane	1.09	para-Xylene	1.00
Pentane	1.04	meta-Xylene	1.04
Hexane	1.03	ortho-Xylene	1.02
Heptane	1.00	1M2-Ethylbenzene	1.02
Octane	0.97	1M3-Ethylbenzene	1.01
Nonane	0.98	1M4-Ethylbenzene	1.00
		1,2,3-Trimethylbenzene	0.98
Unsaturates		1,2,4-Trimethylbenzene	0.97
Acetylene	1.07	1,3,5-Trimethylbenzene	0.98
Ethylene	1.02	Isopropylbenzene	0.97
Hexene-1	0.99	n-Propylbenzene	1.01
Octene-1	1.03	1M2-Isopropylbenzene	0.99
Decene-1	1.01	1M3-Isopropylbenzene	1.01
		1M4-Isopropylbenzene	0.99
		sec - Butylbenzene	1.00
		tert - Butylbenzene	1.02
		n-Butylbenzene	0.98

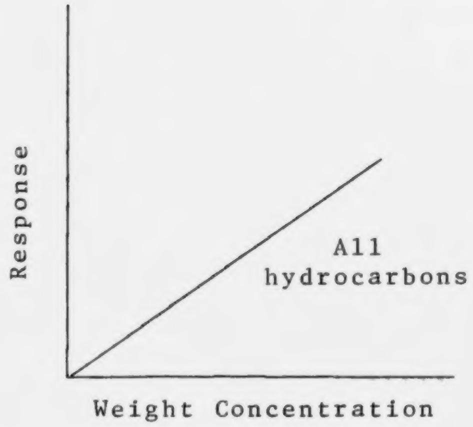


Figure A5-4. Area Response Versus Weight Concentration

5.2.2 Quantitative Analysis

The chromatograph gives a voltage output which changes with time. The simplest device for handling this is the strip chart recorder, which produces a sheet of paper with an inked line on it. The easiest thing to measure is the maximum amount by which the peak departs from the baseline, i.e., peak height. The advantages of this means of quantitation are speed and ease. It is, however, subject to many sources of error. Anything which alters the peak shape will create problems.

Area under the curve does not depend on shape. So long as the same amount of material is injected, even if the column overloads, the same area will be obtained. Operator technique variation, assuming the same amount injected, has essentially no effect on the are figure. Electronic integration is the best approach for measuring area.

Radian uses a gas chromatographic instrument that resolves hydrocarbon mixtures into two peaks. Methane is separated from all other hydrocarbons and passed through the FID and then all other hydrocarbons are passed through the FID simultaneously.

To quantitatively measure methane the following procedure is used. A known volume of sample of known parts per million by weight (ppmw) of methane in air is injected into the analyzer. The peak height is measured. For a single component peak height is an adequate measure of response. A plot of peak height versus ppmw then allows any peak height of an unknown sample to be directly translated into ppmw. The equation of the line shown in Figure A5-5 is:

$$\text{peak height} = (\text{slope})(\text{ppmw}) + \text{intercept}$$

$$\text{intercept} = 0\text{, no material, no response}$$

$$\text{slope} = \frac{\text{peak height of standard material}}{\text{ppmw of standard material}}$$

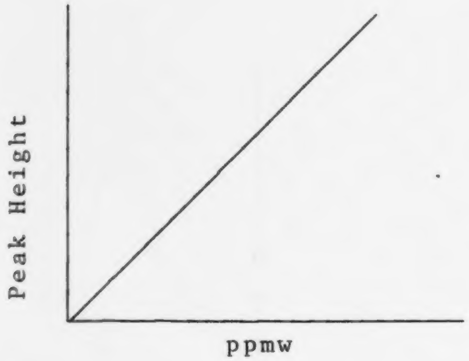


Figure A5-5. Peak Height Versus ppmw

The instrument was calibrated with the standard of known methane so that the slope was identical from day to day or shift to shift.

To quantitatively measure the nonmethane hydrocarbons, a similar procedure was used. A standard of propane of known ppmw in air was used daily to calculate and keep constant the slope of a line similar to that of Figure A5-4. (See Figure A5-6.)

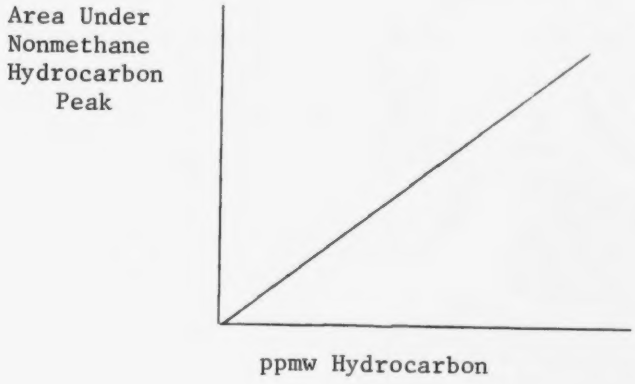


Figure A5-6. Peak Area Versus ppmw Hydrocarbon

Since peak shape changes for different hydrocarbons and the composition in terms of individual hydrocarbons was unknown for the nonmethane peak, peak area versus ppmw was used to calculate nonmethane concentrations. The same weight of any hydrocarbon gave the same peak area (response) within a very few percent. Therefore:

$$\begin{matrix}\text{peak area}\\ \text{(any hydrocarbon)}\end{matrix} = \left(\frac{\text{peak area propane}}{\text{ppmw propane}}\right) \text{ppmw any hydrocarbon}$$

Again the slope of the line was kept constant from day to day and shift to shift by using a standard of known concentration of propane.

Standardization of the THC was accomplished through a separate gas sampling loop without disconnecting the instrument from the sample being analyzed. The instrument was standardized every time it was turned on or once per laboratory shift, whichever was more frequent. The standard contained 100 ppm methane and 100 ppm propane on a molar basis. Repeated tests against other standards have demonstrated the linearity of the response of the instrument.

5.2.3 Calculations

The hydrocarbon emission or leak rate from each sampled source was calculated as a sum of the methane emission rate, the nonmethane gas emission rate, and the organic condensate rate, i.e.,

$$E_T = E_M + E_{NH} + E_L$$

where

E_T = total hydrocarbon emission rate, lb/hr,

E_M = methane emission rate, lb/hr,

E_L = condensed organic liquid rate, lb/hr, and

E_{NM} = nonmethane hydrocarbon emission rate, lb/hr.

The emission rates of methane and nonmethane hydrocarbons may be calculated from the following equation:

$$E_H = K \; {}^{QPM_A} \; (C_s - C_a)_H$$

where

E_H = hydrocarbon emission rate, methane and/or nonmethane, lb/hr,

K = 2.74×10^{-5}, a factor incorporating conversion factors and standard temperature and pressure,

Q = flow rate of gas through the sample train,

P = sampling system pressure at the dry gas meter, psia,

M_A = molecular weight of the air/hydrocarbon mixture, effectively the molecular weight of air,

C_s = concentration of methane/nonmethane hydrocarbon in the gas sample from the sampling train, ppm by weight,

C_a = concentration of methane/nonmethane hydrocarbon in the ambient air, ppm by weight,

$(C_s - C_a)_H$ = methane and/or nonmethane concentration difference between gas and ambient air, ppm by weight, and

The organic condensate rate, E_L, was calculated from the following equation:

$$E_L = \frac{0.115\ V}{t}$$

where,

E_L = organic condensate rate, pounds/hour,

V = volume of condensate collected, ml, and

t = time over which the sample was collected, min.

This calculation assumes an average density of 0.75 g/cc for the organic condensate. The condensate volume was measured, and this density was used to calculate the condensate rate.

5.3 Stack Effluent

Both sulfur gases and particulates are determined by analysis of components from the EPA-5 train. The procedure for preparation of the train for sampling is given prior to description of the specific analyses.

Grap samples were taken from the sampling train using a variety of containers. A description of the preparation of these sampling containers is also given.

5.3.1 EPA-5 Sampling Train Preparation

The following procedures were used to prepare the components of the EPA-5 Sampling Train.

Filter Assembly

1. Dessicate glass-fiber filters for 24 hours.
2. Weigh to the nearest 0.0001 g and place in a labeled, plastic Petri dish for storage.
3. Transfer one filter to the filter assembly and record label number and weight on the field data sheet.
4. Assemble filter and over glassware.

Impinger #1

1. Clean and dry a Smith-Greenburg standard tip impinger.
2. Load with 160 ml 80 percent isopropanol.
3. Weigh entire assembly to ± 0.1 g and record weight on field data sheet.

Impinger #2

1. Clean and dry a modified Smith-Greenburg impinger (open tip).
2. Load with 160 ml 6 percent H_2O_2.
3. Weigh to ± 0.1 g and record weight.

Impinger #3

1. Clean and dry a Smith-Greenburg standard tip impinger.

2. Load with 160 ml 6 percent H_2O_2.

3. Weigh to ± 0.1 g and record.

Impinger #4

1. Clean and dry a modified Smith-Greenburg impinger.

2. Load with 200 g silica gel.

3. Weigh to ± 0.1 g and record.

5.3.2 Particulates Determination

The total weight of the particulates was determined from the combined weight of material collected on the filter, on the exposed surfaces preceeding the filter in the EPA Method 5 sampling train, and in the first impinger. Procedures described in EPA Reference Method 5[1] were used, and a grainloading value was determined based on the total volume of stack gas sampled. These procedures are discussed below.

Probe Rinse (Prefilter Assembly)

1. Rinse all prefilter pieces with acetone into previously tared (± 0.0001 g) 250-ml beakers.

2. Combine probe and nozzle rinse from field with prefilter rinse.

3. Cover beakers with aluminum foil with holes punched in it and allow acetone to evaporate. Finish drying in oven.

4. Weigh beakers and record weights on field data sheets.

Filter

1. Disassemble filter assembly over a clean work surface.

2. Remove filter from fritted glass plate and rubber gasket.

3. Transfer to a labeled Petri dish being very careful not to lose any of the collected particulate.

4. Carefully scrape all fragments of filter adhering to O-ring or glass surfaces onto top of filter paper in the Petri dish.

5. Dessicate 24 hours.

6. Weight filter paper and all fragments to nearest 0.0001 g.

7. Record weight on field data sheet.

Impinger 1

1. Calculate the amount of NH_4OH needed to neutralize all of the H_2SO_4 present in 100 ml of sample.

$$ml_{NH_4OH} = \frac{(V_{S_a} - V_B) \times N_t}{N_{NH_4OH}}$$

$$\times \frac{100}{\text{aliquot taken}}$$

where

V_{S_a} = average volume in ml used for sample titration of SO_3,

N_{NH_4OH} = normality of NH_4OH, given by:

$$\frac{(\%\ \text{from bottle}) \times 10}{17.0} \times 0.90$$

Normality = ~ 14.8

V_B = volume of blank, ml

N_t = normality of titrant, and

Aliquot taken = sample size used in the determination of SO_3.

2. Transfer 100 ml of sample to a 250-ml beaker tared to the nearest 0.0001 g, and carefully

add the calculated volume of NH_4OH to neutralize all H_2SO_4.

3. Evaporate to dryness and reweigh.

4. Calculate the weight of ammonium sulfate present using:

$$g_{(NH_4)_2SO_4} = \frac{(V_S - V_B)}{1000} \times N_t \times \frac{132}{2} \times \frac{100}{\text{aliquot taken}}$$

5. Subtract this value from the net weight of solids to determine the weight of particulate matter in 100 ml of sample.

6. Determine the solids blank by evaporating 100 ml of 80 percent isopropanol from a tared 250-ml beaker and determining the weight of the residue.

7. Subtract the blank from the weight of particulates, then multiply by 4 to get total particulate catch in the first impinger.

5.3.3 Sulfur Oxides (SO_x)

Separate analyses for SO_3 and SO_2 were performed on the impinger samples collected during each EPA Method 5 train operation. Aliquots of the isopropanol (SO_3) and the two

6 percent $H_2O_2(SO_2)$ impingers were titrated with barium perchlorate to a Thorin indicator end point as specified in the EPA Reference Method 8.[2] The amount of sulfate found was used to determine the amounts of SO_3 and SO_2 originally collected from the volume of stack gas sampled.

The SO_2 and SO_3 species are collected respectively in H_2O_2 and 80 percent isopropanol in water, as H_2SO_4. The titration involves the complexing of the barium with the SO_2 and SO_3 which forms a precipitate. When the SO_2 or SO_3 is exhausted, the barium then reacts with the Thorin indicator giving the observed color change.

$$\begin{array}{ll} SO_3 \xrightarrow{H_2O} & \\ & H_2SO_4 + Ba(ClO_4) \rightarrow BaSO_4\downarrow + 2HClO_4 \\ SO_2 \xrightarrow{H_2O_2} & \end{array}$$

When all SO_3/SO_2 is complexed:

$$\underset{\text{(yellow)}}{Ba^{++} + \text{Thorin}} \rightarrow \underset{\text{(peach colored)}}{Ba(\text{Thorin})^{++}}$$

Thorin = [o-(3,6-disulfo-2-hydroxy-1-naphthylazo)-
benzene-arsonic acid]

Reagents

80% Isopropanol

400 ml isopropanol and 100 ml deionized water.

Thorin Indicator

0.20 g Thorin in 100 ml deionized water.

Barium Perchlorate, ~ 0.01 N

1.95 g of $Ba(ClO_4)_2 \cdot 3H_2O$ in 200 ml deionized water. Dilute to one liter with isopropanol.

Sulfuric Acid Standard, ~ 0.01 N

0.14 ml concentrated H_2SO_4 in 500 ml deionized water.

Sodium Hydroxide, ~ 0.01 N

0.040 g NaOH in 500 ml deionized water.

Potassium Acid Phthalate, 0.01 N

0.2041 g KHP in 100 ml deionized water.

Phenolphthalein Indicator

1 g phenolphthalein 95 percent ethyl or isopropyl alcohol and add 50 ml distilled water.

Sample Analysis

A. Standardization

1. Standardize the NaOH to ± 0.0002 N against the KHP using phenolphthalein indicator.

2. Standardize the H_2SO_4 to 0.0002 N against the 0.01 N NaOH using phenolphthalein.

3. Standardize the $Ba(ClO_4)_2 \cdot 3H_2O$ with the 0.01 NH_2SO_4 using Thorin indicator.

B. Impinger 1 - SO_3

Recovery

1. Dry impinger and wipe off any stopcock grease.

2. Weigh entire impinger assembly to the nearest 0.1 g and record weight on field data sheet.

3. Transfer the liquid to a 500 ml graduate.

4. Determine the amount of 100 percent isopropanol to be added by:

   Final Weight of Impinger
   - Tare Weight × 4 = wt isopropanol

5. Rinse the impinger assembly with the calculated amount of 100 percent isopropanol and add to the graduate. Mix the solution well.

6. Dilute to the nearest 50 mls with 80 percent isopropanol, making sure that the final volume is at least 400 mls. Mix; record the final volume on the sample container label.

SO_3 Titration

1. Determine the aliquot size to be used by choosing a quantity which requires 20 - 40 mls of titrant. (Try starting with 1 - 5 ml aliquots and work up.)

2. Pipet the aliquot into an Erlenmeyer flask and add 2 - 4 drops of Thorin indicator solution.

3. Titrate with standardized 0.01 N barium perchlorate to a peach-colored (very light salmon pink) end point.

4. Record volume of titrant used.

5. Repeat procedure until reproducible results are obtained.

6. Retain the rest of the sample for a particulate determination. At least 100 ml must be left.

Blank Titration

1. Pipet the same size aliquot of 80 percent isopropanol into an Erlenmeyer flask and add 2 - 4 drops of Thorin indicator.

2. Titrate as before.

3. Repeat on a second blank sample.

4. Average the results.

C. Impingers 2 and 3 - SO_3

Recovery

1. Dry and weigh impinger assemblies as with Impinger 1 and record the weights on the field data sheets.

2. Transfer contents of each to separate graduated cylinders. These solutions will be handled separately in all succeeding steps.

3. Rinse the connecting tube between Impingers 1 and 2 with deionized water and combine with the No. 2 solution. Repeat for tube between 2 and 3 and add to Solution 3.

4. Dilute each sample to the nearest 50 mls. Record the final volume on the sample container label.

SO_2 Titration

1. Determine aliquot size to be used. (Try starting with around 50 ml of sample of Solution 2.)

2. Pipet this quantity into an Erlenmeyer flask, add the appropriate amount of 100 percent isopropanol (four times the volume of the aliquot taken) and 2 - 4 drops of Thorin indicator. Titrate as before.

3. Repeat procedure with Solution 2 until results are reproducible.

4. Repeat entire procedure with Solution 3.

Blank Titration

1. Pipet the same size aliquot of deionized 80 percent isopropanol in an Erlenmeyer flask, add Thorin indicator and titrate as before.

2. Repeat with a second blank sample.

3. Average the results.

Calculations

A. Calculation of SO_3 Weight

1. To calculate the total weight of SO_3 present in Impinger 1, the following equation was used.

$$\text{grams } SO_3 = \frac{(V_S - V_B) \times N_t \times MW \times 400/\text{aliquot taken}}{1000 \times 2}$$

where

V_S = volume of titrant for sample, in ml,

V_B = volume of titrant for blank, in ml,

N_t = normality of titrant, and

MW = molecular weight of SO_3 (80 g/mole).

Aliquot taken given in ml.

2. Report both determinations.

B. Calculation of SO_2 Weight

1. To calculate the total weight of SO_2 present in each impinger, use equation below:

$$\frac{(V_S - V_B) \times N_t \times MW \times 300/\text{aliquot taken}}{1000 \times 2}$$

where

MW = molecular weight SO_2 (64 g/mole).

2. Report both determinations for Impinger 2 and Impinger 3.

5.3.4 Nitrogen Oxides

Nitrogen oxides are converted to nitric acid by the sorbent solution and the resulting nitrate ion is determined colorimetrically.

5.3.4.1 Determination of Nitrogen Oxides - Phenoldisulfonic Acid Method[3]

Nitrogen oxides (NO and/or NO_2, or collectively, NO_x) in stack gas are determined as nitrate (NO_3^-) colorimetrically. NO_x is collected in a glass flow-through type bomb and converted to nitrate ion by reaction with aqueous hydrogen perioxide which is injected immediately following collection of the sample. A yellow color is developed at a later time by the addition of reagents. The color intensity developed is a function of the concentration of the nitrate. The intensity is measured using a spectrophotometer capable of operating at 410 nM.

This method may be used for stack sampling with a varying ratio of NO to NO_2. Inorganic nitrates, nitrites, and organic nitrogen compounds easily oxidized to nitrate ion may interfere and give high results. Reducing agents such as SO_2 and halides may interfere to give lower results. The range of analysis is from 0.5 μg NO_2/ml of solution to 50.0 μg NO_2/ml of solution.

Instrumentation

A Bausch and Lomb Spectronic 21 spectrophotometer was used.

Reagents

All reagents should be ACS reagent grade.

A. Potassium Hydroxide (12 N)

Using distilled water, dissolve 673 grams of potassium hydroxide (KOH) in a 1000 ml volumetric flask and make up to the mark.

B. Phenoldisulfonic Acid

Dissolve 75 grams of pure phenol in 450 ml of concentrated sulfuric acid (H_2SO_4). Add 25 ml of fuming H_2SO_4 (15 percent free SO_3). Stir well; heat for two hours on a steam bath. This reagent is stable and can be stored for as long as desired.

C. Stock Nitrate Solution

Dissolve 0.4359 grams of anhydrous potassium nitrate (KNO_3) in distilled water in a 500 ml volumetric flask. Fill up to the mark. This solution contains the equivalent of 400 μg NO_2/ml. Dilutions from this are used to make the working solution.

D. Absorbing Reagent (0.1 $\underline{M}$ H_2O_2 in 0.05 $\underline{M}$ H_2SO_4)

Prepare by adding 2.8 ml concentrated H_2SO_4 and 10.0 ml 30 percent H_2O_2 to 500 ml deionized water in a 1000 ml volumetric flask. Dilute to 1.0 liter with distilled or deionized water. (Caution: do not mix acid and peroxide before dilution.)

Preparation of Standard Curve

Place 25 ml of stock nitrate solution in a porcelain crucible and evaporate to dryness on a steam bath. Add 2.0 ml of phenoldisulfonic acid and heat gently on the steam bath until all residue has dissolved. Using distilled water, rinse this solution into a 200 ml volumetric flask and make up to the mark. This standard solution now contains the equivalent to 50 μg NO_2/ml. Pipet 0, 1, 2, 3, 5, 7, 8, and 10 ml of the 50 μg NO_2/ml into 50 ml volumetric flasks. Add 2.0 ml of phenoldisulfonic acid to each flask and dilute each with approximately 20 ml of distilled water. To each flask add 9.0 ml of KOH (12 N) and make up to 50 ml with distilled water. The equivalent μg NO_2/ml in each volumetric flask is:

0 ml = 0.0 µg NO_2/ml = blank
1.0 ml = 1.0 µg NO_2/ml
2.0 ml = 2.0 µg NO_2/ml
3.0 ml = 3.0 µg NO_2/ml
5.0 ml = 5.0 µg NO_2/ml
7.0 ml = 7.0 µg NO_2/ml
8.0 ml = 8.0 µg NO_2/ml
10.0 ml = 10.0 µg NO_2/ml

Mix thoroughly. Any precipitate formed need not be filtered out as it settles to the bottom and should not interfere. (The solution may be filtered, if desired.) Using 10 mm cuvette, measure the absorbance of each standard against the reagent blank at 410 nM. Plot a curve of absorbance versus µg NO_2/ml.

Sample Analysis

Empty contents of sample bomb into a 100 ml volumetric flask. Rinse bomb twice with approximately 10 ml portions of distilled or deionized water into the volumetric flask. Add 1.0 N KOH dropwise until sample is slightly alkaline to litmus paper. Fill to the mark with distilled water and mix well. Samples are stable at this point although they may slowly evolve oxygen. Place a 10 ml aliquot of this solution in a porcelain crucible and evaporate to dryness on a steam bath. Dissolve the residue in 2.0 ml of phenoldisulfonic acid. Using distilled or deionized water, rinse this solution into a

50 ml volumetric flask and make up to approximately 30 ml. Add 9.0 ml KOH (12 N) and bring the volume up to 50 ml. Mix thoroughly. Measure the resulting absorbance at 410 nM and determine the μg NO_2/ml from the prepared standard curve.

Calculations

The amount of NO_2 in the original sample can be calculated:

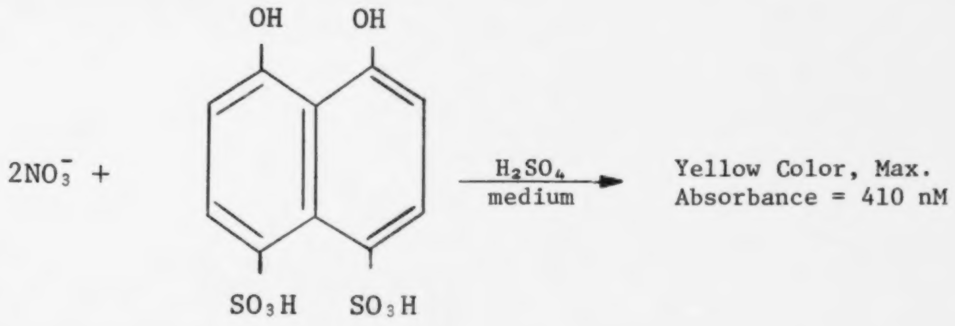
$$\mu g\ NO_2 = \frac{(\mu g\ NO_2/ml)(\text{dilution volume})(\text{sample volume})}{(\text{aliquot volume})}$$

$$= \frac{(\mu g\ NO_2/ml)(50\ ml)(100\ ml)}{10\ ml}$$

Note that NO_x is reported as equivalent of NO_2.

5.3.4.2 Method for Low Concentrations of Nitrate: Spectrophotometric Using Chromotropic Acid[4]

In this method a 2-ml nitrate sample is mixed with masking reagents and chromotropic acid indicator in a sulfuric acid medium.



The absorbance of the yellow reaction product is measured in a 1-cm cell at 410 nM. The nitrate concentration is calculated by comparing the absorbance to that of a known nitrate standard.

This procedure is designed to measure nitrate ion in solutions which contain 10 to 60 ppm nitrate.

Ferric ion in excess of 50 ppm and chloride ion in excess of 2400 ppm (0.07 molar) interfere. Cr^{+3} in excess of 20 ppm interferes.

Oxidizing substances and nitrite ion are eliminated by the use of sodium sulfite-urea solution. Suspended solids which do not dissolve in sulfuric acid interfere and must be removed by filtration or centrifugation.

The accuracy of this procedure is ± 3 percent for nitrate concentrations ranging from 0.00016 to 0.0003 molar (10 - 20 ppm), and ± 2 percent for the 0.0003 to 0.001 molar (20 - 60 ppm) range. Samples containing nitrate concentrations in excess of 0.001 molar (60 ppm) should first be diluted before this procedure is used. At least one nitrate standard of similar concentration should be run with the nitrate samples.

The purity factor of the chromotropic acid reagent is important. The absorbance read for the blank should be less than 0.018, especially for measuring nitrate concentrations in the 1 - 20 ppm range. Better reproducibility is also obtained when freshly recrystallized chromotropic acid is used.

Instrumentation

A Bausch and Lomb Spectronic 21 spectrophotometer was used.

Reagents

A. 1000 ppm Standard Nitrate Stock Solution

Accurately weigh and dissolve 1.371 g of reagent grade sodium nitrate in about 60 ml of distilled water. Transfer the solution quantitatively to a one liter volumetric flask and dilute to volume with distilled water. This solution will be used to prepare a standard for comparing nitrate samples.

B. 20 ppm Standard Nitrate Solution

Pipet 10.00 ml of the 1000 ppm nitrate stock solution into a 500 ml volumetric flask and dilute to volume with distilled water. This solution is convenient for comparing the concentrations of nitrate samples.

C. Sulfuric Acid

Concentrated reagent grade sulfuric acid is used in this procedure. It whould be free of nitrate ion.

Caution!!! Care should be taken when handling this reagent. Avoid contact with the skin and clothes. Rinse immediately if spilled.

D. 0.1 Percent Chromotropic Acid Solution

Dissolve 0.18 g of freshly recrystallized chromotropic acid in 100 ml of concentrated sulfuric acid. This solution is light sensitive and should be stored in low actinic bottles. The solution should vary from colorless to a slight yellow tinge, and is adequately stable for two weeks.

A detailed procedure for the recrystallization of chromotropic acid is given at the end of this section.

E. Sodium Sulfite - Urea Solution

Dissolve 4 g of sodium sulfite and 5 g of urea in 100 ml of distilled water. This solution should be mixed on the same day it is used.

F. Antimony Sulfate Solution

Dissolve 1.0 g of antimony metal in 160 ml of concentrated sulfuric acid by heating and stirring on a hot plate (~ 100°C). Cool and slowly add the solution to 40 ml of cold distilled water. Any salt which crystallizes when the solution is being stored may be redissolved by mild heating.

Recrystallization of Chromotropic Acid

The 0.1 percent chromotropic acid solution needed in the procedure requires purified chromotropic acid. A recrystallization procedure is as follows:

A. Prepare a saturated solution of disodium salt of 1,8-dihydroxy-3,6-naphthalene disulfonic acid in distilled water. This may be done by dissolving 10.0 grams of the above salt in 45 ml of distilled water using a 100 ml graduated beaker. Mild heating (~ 40°C) and stirring may be used to hasten dissolution. The resultant solution is black.

B. Add one or two spatulas of decolorizing charcoal and stir for five minutes.

C. Using a suction filter, remove the charcoal and undissolved solids and save the filtrate. The filtrate will still have a dark color. Care should be taken not to dilute the filtrate.

D. Add concentrated sulfuric acid dropwise while stirring in a 100 ml graduated beaker, such that the temperature remains less than 50°C. The amount of sulfuric acid added should be 35 percent of the original volume.

E. Crystallization will occur within one hour, and the yield should be about 50 percent of the original weight dissolved. The beaker may be cooled in ice water. However, similar results are obtained if the solution is allowed to cool at room temperature.

F. Separate the crystals from the supernatant liquor with a medium-frit, glass suction funnel (~ 30 ml capacity). Wash the crystals with reagent-grade ethanol about four times or until the filtrate is free from yellow color.

G. Transfer the crystals to a clean, dry 50 ml beaker and dry for six hours at 60°C. The crystals will be finely divided and have a light gray appearance.

H. Store the dried crystals in a dark bottle. The time of storage should not exceed two months unless the precaution is made to store the crystals in an inert atmosphere.

Sample Analysis

A. Pipet 2.00 ml of nitrate solution (standard or sample) having a nitrate content in the range 1 - 60 ppm into dry 10 ml volumetric flasks.

B. Add 1 - 2 drops of the sodium sulfite-urea solution prepared in (5).

C. Add 8 - 10 drops (0.5 ml) of distilled water and swirl gently. This step offers an opportunity to thoroughly rinse the lips of the volumetric flasks.

Note: The percent water is critical in this procedure and should range from 27 - 31 percent by volume. If the volumetric flasks are not dry for step (1), then less water should be added in step (3).

D. Add 2 ml of the antimony sulfate solution and swirl. Allow the mixture to cool. A tray of cold water at 10 - 20°C in which the water level is slightly above that in the flasks may be used for cooling purposes.

Note: Heat developed during mixing has no harmful effect. A cooling bath is not necessary if the flasks are allowed to stand at room temperature for at least 15 minutes. Care should be taken, however, to dissipate sufficient heat to avoid boiling of the solutions.

E. Add 1.0 ml of the chromotropic acid solution. Swirl the flasks again and allow them to cool.

F. Add concentrated sulfuric acid to adjust the volume to the 10 ml mark, stopper the flasks and mix the contents by inverting them about four times. Allow the solutions to stand for 45 minutes at room temperature.

Adjust the volume to the 10 ml mark again with concentrated sulfuric acid. Final mixing should be done gently so as not to introduce gas bubbles.

G. The adsorbance reading should be taken 15 minutes or more after the final adjustment of volume.

Rinse the 1-cm cell with the solution and then fill it about 2/3 full. For this operation it was found expedient to use a 25-ml beaker to hold the cell in a slanting position with a ground side facing up and pouring the solution slowly down the side of the cell. Rinse the outside of the cell by partially dipping the cell in a water bath and wiping it with a moist paper tissue. Place the cap on the cell and wipe clean with a dry tissue.

Read the absorbance at 410 nM in a suitable spectrophotometer, using 625 nM as the base line. A blank (distilled water substituted for nitrate sample) should also be prepared and used as the reference cell or read separately.

Calculations

$$C_D = C_S \frac{A_U - A_B}{A_S - A_B}$$

where

C_S = concentration of standard solution ($\text{mg } NO_3^-$/liter),

A_U = absorbance of unknown solution (absorbance units),

A_B = absorbance of blank solution (absorbance units),

A_S = absorbance of standard solution (absorbance units),

C_D = concentration of nitrate in solution used (mg/ℓ).

Calculation for Concentration of NO_3^-

$$\text{ppm } NO_3^- = \frac{\text{conc. } NO_3^- \text{ std. (ppm)}}{\text{Abs. of std.}} \times \text{Abs. of sample}$$

$$\frac{\text{ppm } NO_3^-}{10} = \text{mg of } NO_3^- \text{ in 100 ml sorbent}$$

Calculation for NO_x Concentration in Gas Phase

$$\text{ppm } NO_x = \frac{1}{B} \times \frac{10^3}{62} \text{ (mg } NO_3^- \text{ found in gas sample)}$$

where

$$B = \frac{(\text{B.P.} \pm \text{M.R.})[\text{Vol(flask)} - \text{Vol(sorbent)}]}{62{,}322\ (^\circ\text{K})}$$

where

B.P. = barometric pressure in mm Hg,

M.R. = manometer reading in mm Hg = mm H_2O (1/13.6): positive value if flask gas pressure is greater than atmospheric pressure, negative value if otherwise,

Vol(flask) = volume of gas flask in ml,

Vol(sorbent) = volume of sorbent placed in gas flask (15 ml),

°K = room temperature in degrees Kelvin.

Example Calculation

B.P. = 740 mm Hg

Temp = 23°C

M.R. = 21.5 mm H_2O

Vol flask = 2055 ml

2.0 mg NO_3^-

$$B = \frac{(740 - 21.5/13.6)(2055-15)}{(62{,}322)(296)} = 0.0817$$

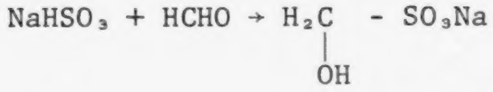
$$\frac{2.0 \times 10^3}{0.0817 \times 62} = 395 \text{ ppm } NO_x$$

5.3.5 Aldehydes[9]

The one percent bisulfite impinger solutions were analyzed using an iodine-starch titration. Samples were collected, diluted to 50 ml and treated with 10 ml of bisulfite and 1 ml starch indicator. Any excess bisulfite was then destroyed with an excess of 0.1 N iodine. The excess iodine was then destroyed with a few drops of sodium thiosulfate. The thiosulfate was then titrated to a faint blue endpoint. Addition of 25 ml of carbonate buffer solution released the complexed bisulfite which was titrated to a final endpoint with 0.01 N iodine.

This procedure measures total aldehydes as formaldehyde. One ml of 0.01 N iodine is equivalent to 0.15 mg of formaldehyde. By accurately measuring the amount of titrant used in the final titration only, the total mg of aldehyde may be calculated.

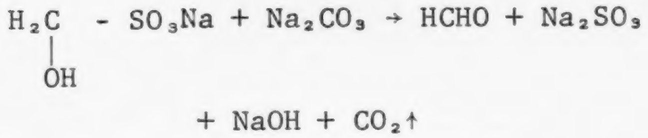
The aldehyde impingers are each filled with 20 ml of fresh one percent sodium bisulfite. The aldehydes are collected in the sodium bisulfite solution forming an aldehyde bisulfite complex. When the sample is assayed, the first step is to destroy the excess bisulfite with an excess of iodine. The excess iodine is then destroyed by the addition of thiosulfate and the thiosulfate is titrated to a faint blue endpoint. Addition of a carbonate buffer solution releases the complexed bisulfite which is then titrated to a final endpoint. This procedure is described by the equations below.

- 

  $NaHSO_3 + HCHO \rightarrow H_2\underset{\underset{OH}{|}}{C} - SO_3Na$

- $NaHSO_3 + I_2 + H_2O \rightarrow NaI + H_2SO_4 + HI$

- $4I_2 + Na_2S_2O_3 + 5H_2O \rightarrow 2NaI + 2H_2SO_4 + 6HI$

- 

  $H_2\underset{\underset{OH}{|}}{C} - SO_3Na + Na_2CO_3 \rightarrow HCHO + Na_2SO_3 + NaOH + CO_2\uparrow$

- $Na_2SO_3 + I_2 + H_2O \rightarrow 2NaI + H_2SO_4$

Reagents

A. Iodine, 0.1 N (Approximate)

Dissolve 25 g of potassium iodide in about 25 ml of deionized water. Add 12.7 g of iodine and dilute to one liter.

B. Iodine, 0.01 N

Dilute 100 ml of the 0.1 N iodine solution to one liter. Standardize against 0.05 N sodium thiosulfate using starch indicator.

C. Sodium Thiosulfate, 0.05 N

Dissolve 1.24 g of sodium thiosulfate in 100 ml of deionized water.

D. Starch Solution, 1 Percent

Make a paste of 1 g of soluble starch and 2 ml of water. Slowly add the paste to 100 ml of boiling water. Cool and add a few ml of chloroform as a preservative. Store in a stoppered bottle. Discard when mold growth is noticeable.

E. Sodium Bisulfite, 1 Percent

Dissolve 1 g of sodium bisulfite in 100 ml of water. This should be freshly prepared each week.

F. Sodium Carbonate Buffer Solution

Dissolve 80 g of anhydrous sodium carbonate in about 500 ml of water. Slowly add 20 ml of glacial acetic acid and dilute to one liter. Store in refrigerator.

Sample Analysis

A. Dilute each sample to a final volume of 50 ml.

B. Pipet a 5 ml aliquot of the sample into a 125 ml Erlenmeyer flask.

C. Add 10 ml of one percent sodium bisulfite and one ml of one percent starch solution.

D. Titrate with 0.1 N iodine to a dark blue color.

E. Destroy the excess iodine with a few drops of 0.05 N sodium thiosulfate.

F. Add 0.01 N iodine until a faint blue endpoint is reached. (The excess inorganic bisulfite is now completely oxidized to sulfate. The solution is now ready for the assay of the aldehyde bisulfite addition product.)

G. Chill a flask in an ice bath and add 25 ml of chilled sodium carbonate buffer.

H. Titrate the liberated sulfite with 0.01 N iodine, using a microburet, to a faint blue endpoint. The amount of iodine used in this step must be accurately measured and recorded.

I. Repeat the procedure until reproducible results are obtained.

J. For each set of samples, a blank should be run using 5 ml of deionized water.

Calculations

One ml of 0.01 N iodine is equivalent to 0.15 ml of formaldehyde. Determine the mg of formaldehyde equivalent to one ml of standardized iodine.

$$\frac{0.01\ \text{N}}{0.15\ \text{mg}} = \frac{\text{Normality of iodine used (0.01)}}{\text{Equivalent mg of formaldehyde}}$$

$$\text{Total } \mu\text{g aldehyde} = \frac{(V_S - V_B) \times \text{mg}_{CH_2O} \times V_T \times 10^3}{\text{Aliquot Taken}}$$

where

V_S = ml of 0.1 N I used in sample,

V_B = ml of 0.01 N I used in blank,

V_T = total volume to which sample was diluted (50 ml),

mg_{CH_2O} = equivalent mg of formaldehyde as determined from equation.

5.3.6 Ammonia[5]

Ammonia in the gas stream is collected by bubbling the gas through impingers containing sulfuric acid at a $pH < 2$. Ammonia is determined by a distillation-titration method in which the sample is buffered to a pH of 9.5 by using sodium hydroxide and a sodium tetraborate buffer. The sample is then placed in a distillation flask with the ammonia being driven off and bubbled through an indicating boric acid scrubbing solution. This scrubbing solution changes color upon reaction with the ammonia. The amount of ammonia present is quantified by a titration technique utilizing a standard sulfuric acid solution to titrate back to the indicator's original color.

The sampling train is prepared according to the following procedure:

1. Pour 250 ml 0.1 N H_2SO_4 into each of three impingers with standard Smith Greenburg tips. Weigh and record weight and volume.

2. Weigh and record the combined weight of impinger and 1/2 silica gel.

3. Prepare hot half of EPA 5 box as with EPA 5 run. It is not necessary to weigh the filter.

4. Connect impingers and glassware as in EPA 5 run.

Reagents

A. Borate Buffer Solution

Combine 88 ml 0.1 N NaOH with 500 ml 0.025 M sodium tetraborate and dilute to 1 ℓ. Make tetraborate solution by dissolving 5.0 g $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10\ H_2O$ and dilute to 1 ℓ.

B. Sodium Hydroxide (6N NaOH)

Dissolve 240 g NaOH pellets in 1 ℓ distilled water.

C. Sodium Hydroxide (1N NaOH)

Dilute one volume 6N NaOH in five volumes distilled water.

D. Sulfuric Acid (1N H_2SO_4)

Add 28 ml concentrated sulfuric acid to 500 ml distilled water and dilute to one.

E. Phenolphthalein Solution

Dissolve 1 g phenolphthalein in 50 ml 95 percent ethyl or isopropyl alcohol and add 50 ml distilled water.

F. Sodium Thisosulfate

Solid $Na_2S_2O_3 \cdot 5H_2O$, C.P., for complexing mercury.

G. Mixed Indicator Solution

Prepare this reagent monthly. Dissolve 200 mg methyl red indicator in 100 ml 95 percent ethyl or isopropyl alcohol. Dissolve 100 mg methylene blue in 50 ml 95 percent ethyl or isopropyl alcohol. Combine the two solutions.

H. Indicating Boric Acid Solution

Dissolve 20 g H_3BO_3 in distilled water; add 10 ml mixed indicator solution, and dilute to 1 ℓ. Prepare fresh monthly.

I. Standard Sulfuric Acid Titrant (0.02N)

0.02 N, 1 ml is equivalent to 0.28 mg NH_3-N, Dilute 3.0 ml concentrated H_2SO_4 to 1 ℓ to make approximately 0.1 N acid. Dilute 200 ml 0.1 N acid to 1 ℓ. Standardize against 0.05 N Na_2CO_3 prepared by drying anhydrous sodium carbonate at 140°C for four hours, cooling in a dessicator, and transferring 2.5 g to a 1 ℓ flask and diluting to volume. Take 20 ml of sodium carbonate solution, add about 80 ml distilled water, titrate with the sulfuric acid solution to a pH of about 5. Lift out the electrode, rinse into the beaker, transfer the beaker to a hot plate, cover with a watch glass and boil gently for 3 - 5 minutes. Cool, rinse watch glass into beaker, and finish the titration to the pH inflection point. Calculate normality as:

$$N = \frac{A \times B}{53.0 \times C}$$

where

A = g Na_2CO_3 weighed into 1 ℓ

B = ml Na_2CO_3 used in titration (i.e., 20 ml)

C = ml acid used.

Adjust the acid solution as necessary until N = 0.020.

Sample Analysis

A. Preliminary Distillation

1. Prior to beginning a set of analyses steam out the distillation apparatus. Place 500 ml distilled water in a Kjeldhal flask, add 20 ml borate buffer and a few glass beads; adjust pH to 9.5 with 6N NaOH. Boil for about 1/2 hour until the distillate

shows no traces of ammonia. Leave the entire distillation apparatus assembled until just prior to starting sample distillation.

2. Use 350 to 500 ml of sample or a portion diluted to that volume. Add 25 ml borate buffer and adjust the pH to 9.5 with 6N NaOH. Check the pH with a meter on every sample. Some samples may contain high ammonia concentrations, in which case adjust the pH to about 9.7. Check the pH after distillation to ensure it did not drop below 9.5. Add several drops of phenolphthalein indicator to observe pH during distillation; the color should remain deep red if the pH stays at 9.5.

3. Add 0.2 g sodium thiosulfate if the sample was preserved with mercury.

4. Transfer the sample to a Kjeldhal flask and place on the distillation apparatus. Add 50 ml indicating boric acid solution to a 500 Erlenmeyer flask. Place the condenser outlet tip below the surface of the receiving boric acid solution.

5. Distill at a rate of 6 - 10 ml per minute until 250 ml or more of distillate has been collected. Then lower the distillate until the outlet tip is free of contact with the distillate and continue to steam out for about 5 minutes to cleanse the condenser and delivery tube.

6. Leave the Kjeldhal flasks in place until just prior to running the next set of samples.

B. Titration

1. Distill samples as described above using indicating boric acid as an absorbent.

2. Titrate the distillate with 0.02 N H_2SO_4 to a pale lavender color. Carry a distilled water blank through all the steps.

3. The analyst should periodically test procedures by preparing standard solutions of ammonium chloride. A recovery of $\geqslant 97$ percent should be expected.

Calculations

$$\text{mg/l } NH_3\text{-N} = \frac{(A - B) \times 280}{\text{ml sample}}$$

where

A = ml H_2SO_4 for sample,

B = ml H_2SO_4 for blank.

5.3.7 Hydrogen Cyanide[5]

Cyanide in the gas stream is collected by bubbling the gas through impingers containing sodium hydroxide at a $pH > 12$. The resulting impinger solutions are tested for the presence of oxidizing agents, which if found are removed by the addition of ascorbic acid. The solutions are also tested for the presence of sulfide, which is precipitated using lead nitrate and filtered off. An aliquot of sample is then placed in a cyanide distillation apparatus and an air purge is applied with a vacuum. The sample is acidified using sulfuric acid with the resultant off-gases being collected in a bubbler containing a solution of sodium hydroxide. This distillation is used to separate CN^- from other cyano compounds. The concentration of CN^- in the scrubber solution is then determined by colorimetric determination using pryidine-barbituric acid, which forms an intense blue color with free cyanide. The absorbance is then read and concentrations determined against standards. These concentrations are calculated as hydrogen cyanide.

Instrumentation

A Bausch and Lomb Spectromic 21 spectrophotometer was used.

Reagents

A. Sodium Hydroxide Solution (1.25 N)

Dissolve 50 g NaOH in distilled water, dilute to 1 ℓ.

B. Magnesium Chloride Reagent

Dissolve 510 g $MgCL_2 \cdot 6H_2O$ in water, dilute to 1 ℓ.

C. Sulfuric Acid, 1:1

Very slowly add 1 part concentrated sulfuric acid to one part distilled water.

D. Chloramine-T Solution

Dissolve 1.0 g chloramine-T powder in 100 ml distilled water. Prepare weekly; store in refrigerator.

E. Stock Cyanide Solution

Dissolve 10 g NaOH and 2.51 g KCN in 1 ℓ distilled water. Make this solution fresh each time a new standard curve is developed. 1 ml = 1 mg CN.

F. Standard Cyanide Solution

Dilute 10.00 ml of stock cyanide solution to 1 ℓ with 0.25 N NaOH; 1 ml = 10 μg CN. Make a dilution of 10 ml diluted to 100 ml; 1 ml = 1 μg CN. Prepare fresh daily.

G. Pyridine-Barbituric Acid Reagent

Place 15 g barbituric acid in a 250 ml volumetric flask; wash down the sides of the flask with distilled water, wetting the barbituric acid just slightly. Add 75 ml pyridine and mix well; add 15 ml concentrated HCI and mix well. Attempt to dissolve as much of the barbituric acid as possible by vigorous shaking. When cool, dilute to volume (250 ml) with distilled water. It may be necessary to let the reagent stand a short while or to warm the flask slightly by rinsing with hot water to dissolve all the barbituric acid. When properly prepared, the reagent should be pale-yellow with no turbidity. Afterwards, if a precipitate should develop, make up a new reagent. Store in a dark bottle and refrigerate; prepare monthly.

H. Sodium Dihydrogen Phosphate, 1 M

Dissolve 135 g $NaH_2PO_4 \cdot H_2O$ in 1 ℓ distilled water; refrigerate.

I. Sodium Hydroxide Solution, 0.25 N

Dissolve 10 g NaOH in 1 ℓ distilled water.

Sample Analysis

The sample preservation procedure consists of raising the pH to 12.0 - 12.5. If the sample does not contain excessive alkalinity, filter (Whatman No. 40 or equivalent), and raise the pH to 12.0 - 12.5 with strong NaOH solution or with NaOH pellets. Any precipitate which forms at this step will redissolve upon acidification during analysis. If the sample does contain high alkalinity (i.e., high total inorganic carbon), the dissolved CO_2 must be removed to eliminate interferences during sample distillation. Raise the pH to 12.0 - 12.5 with $Ca(OH)_2$ causing calcium carbonate to precipitate. Let the precipitate settle, draw off clarified supernatant and filter

(Whatman No. 40 or equivalent). Always check sample pH with a glass electrode or short-range pH paper.

A. Distillation

1. Wash thoroughly, rinse, and assemble the distillation apparatus.

2. Add 50 ml of 1.25 N NaOH to the gas washer. Fill to about one inch below the ground glass joint with distilled water.

3. Ensure that all ground glass joints are seated well.

4. Turn on the vacuum pump; air will be drawn into the gas washer via the distillation flask.

5. Turn on the cooling water.

6. If for some reason samples were not preserved against sulfide and then filtered, do so now.

7. Measure 250 ml of sample, pour slowly into the thistle tube, and allow the vacuum to draw the sample into the distillation flask.

8. Adjust the needle valve to give an air flow rate of about two bubbles per second entering the distillation flask.

9. Slowly add 50 ml 1:1 H_2SO_4 through the thistle tube.

10. Add 20 ml magnesium chloride reagent.

11. Turn power on to the heating mantle. Adequate refluxing is indicated by 40 - 50 drops per minute forming from the condenser. Vapors should not rise more than half way up the condenser. Avoid excessively vigorous boiling.

12. Reflux for one hour; turn off heat and continue the air flow for 15 minutes.

13. Turn off the vacuum and drain the scrubbing solution into a 250 ml (Volumetric) flask. Rinse the connecting tube and gas washer with distilled water. Add the rinse water to the (Volumetric) flask.

14. Dilute the drained fluid to 250 ml with distilled water. If the solution is not analyzed immediately for CN, store in the refrigerator and analyze within four days.

B. Colorimetric Determination

1. Turn on the spectrophotometer and set the wave length to 578 nM. Allow the instrument to warm up for 15 minutes. Adjust zero absorbance on the instrument each time it is used by preparing a reagent blank.

2. Take 20 ml of absorption liquid and place in a 50 ml Nessler tube. The colorimetric method is best for samples containing 3 - 9 μg CN in 20 ml. If necessary use a smaller volume of absorption liquid and dilute to 20 ml with 0.25 N NaOH.

3. Add 15 ml phosphate buffer and invert the tube to mix well before proceeding to Step 4.

4. Add 2.0 ml chloramine-T solution, and again invert the tube to mix well, proceed within 30 seconds to Step 5.

5. Add 5 ml pyridine-barbituric acid; invert the tube and mix well. Mark the time.

6. Add distilled water to give a final volume of 50 ml. Mix well; let the color develop for exactly 10 minutes.

7. Measure the absorbance at 578 nM against a reagent blank prepared by taking a 20 ml sample of 0.25 N NaOH through the color development procedures.

8. As a quality control measure the distillation apparatus, reagents, and other potential sources of error should be periodically tested. A minimum of 98 percent recovery from a 1 mg/ℓ CN standard should be expected.

C. Standardization

1. Use the 0.25 N NaOH solution to prepare a blank and to make dilutions; use the standard 1 ml = 1 μg CN solution to prepare a series of standards. Pipet into a series of six Nessler tubes 0.0 (blank), 2.00, 4.00, 6.00, 8.00, and 10.00 ml of the standard CN solution. Follow in the same order with 20.0, 18.0, 16.0, 14.0, 12.0 ml and 10 ml of 0.25 N NaOH to make a series of 20 ml samples.

2. Proceed with Steps 3 - 7 above using 1 cm spectrophotometer cells. Plot absorbance (y-axis, ordinate) against μg CN (x-axis, abscissa). The slope should be in the vicinity of 0.065 - 0.075 per μg.

Calculations

$$\text{CN (mg/1)} = \frac{A \times B}{C \times D}$$

where

A = μg from absorbance curve,

B = total ml absorbing solution used in the distillation (i.e., 250 ml), C = ml original sample (i.e., 250 ml unless a smaller portion was used and diluted to 250 ml),

D = ml absorbing solution used in the color development (20 ml or less).

5.4 Nonbaggable Sample Analyses

5.4.1 Oil

The oil layer samples are assayed by placing 2 ml of oil into an open container. The sample is stirred for eight hours which allows the volatile material in the sample to evaporate. The volatiles content is represented by the change in the sample weight over the test period.

Calculation of volatile organics in an oil sample can be accomplished with the equation below:

$$VO = \frac{\Delta_w}{w_i}$$

where

VO = weight fraction of volatiles in sample,

Δ_w = initial sample weight - final sample weight,

w_i = initial sample weight.

The emission rate of volatile hydrocarbons from oil can be calculated using the following equation.

$$ER_{oil} = \frac{G(VO_i - VO_o)}{1 - VO_i}$$

where

ER_{oil} = emission rate of hydrocarbon in lb/hr,

G = flow of weathered oil in lb/hr,

VO_i = weight fraction of volatiles in inlet oil,

VO_o = weight fraction of volatiles in outlet oil.

5.4.2 Water

Wastewater samples are analyzed for the amount of purgeable organics. The basis for the analysis is that only the volatile components in the wastewater collection and treatment systems will be lost as fugitive emissions. These volatile compounds comprise the bulk of the purgeable organics in the liquid.

The purgeable organics are swept out of the water into a Teflon sampling bag. At the conclusion of the purging cycle, the contents of the Teflon bag are analyzed on the Total Hydrocarbon Analyzer as previously described. The equipment for this analysis is organized as shown in Figure A5-7. The bag is a standard Teflon sampling bag. The purge gas for the Bellar unit is zero grade nitrogen with a flow rate of approximately 30 ml/min. The flow rate is controlled with two needle valves but will vary slightly from sample to sample and must

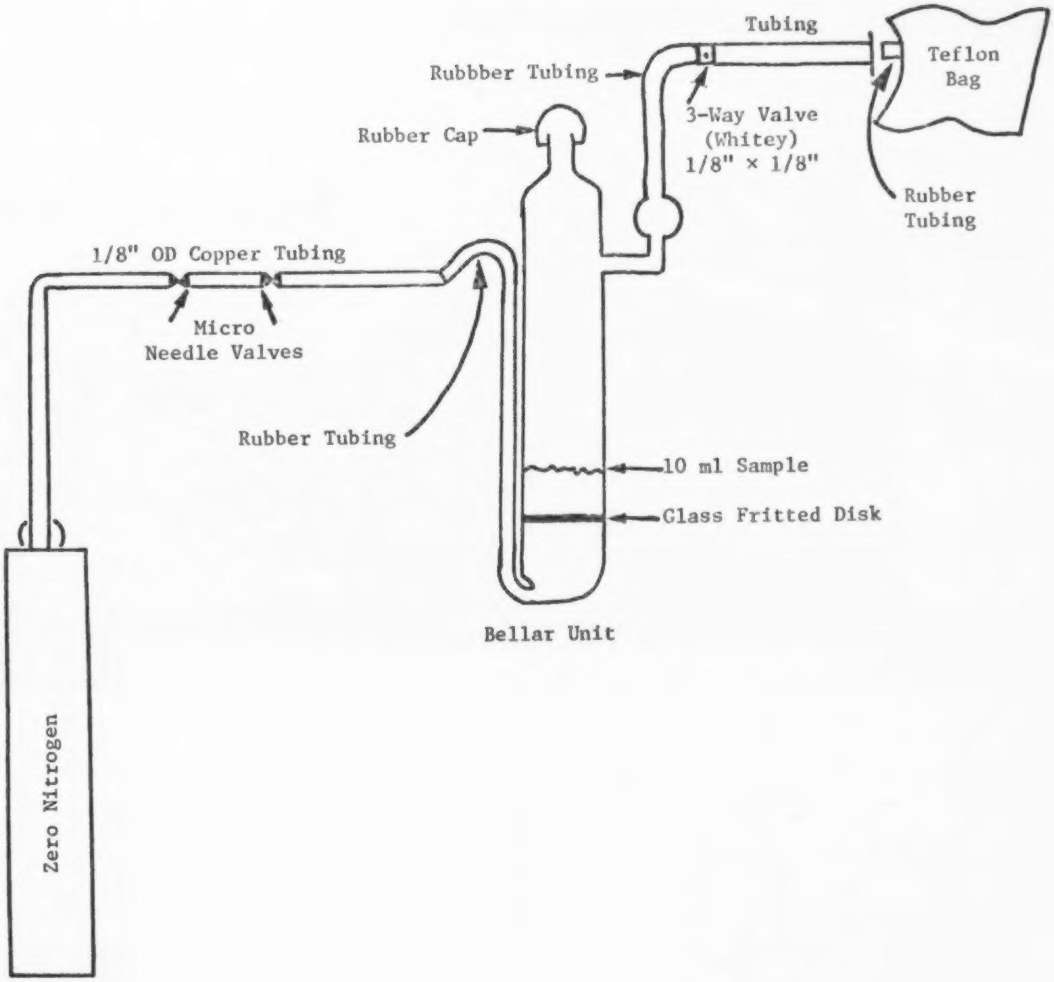

Tubing
Teflon Bag
Rubbber Tubing
Rubber Cap
3-Way Valve (Whitey) 1/8" × 1/8"
Rubber Tubing
1/8" OD Copper Tubing
Micro Needle Valves
Rubber Tubing
10 ml Sample
Glass Fritted Disk
Bellar Unit
Zero Nitrogen

Figure A5-7. Wastewater Purge Apparatus

be measured each time using a bubble meter on the downstream side of the Bellar apparatus. Purging is continued for approximately 30 minutes. The Bellar apparatus requires thorough cleaning between samples. The Teflon bag must be thoroughly flushed with zero grade nitrogen between each sample and a blank sample is analyzed for total hydrocarbons at the end of the flushing cycle.

The volatile hydrocarbon content of the water can be calculated from the following equation:

$$VO = (FR)(time)(ppmw)(P_{purge\ gas})(10^{-6})$$

where

VO = volatile organics, grams,

FR = purge flow rate, ml/min,

time = time of purge, min,

ppmw = concentration of total hydrocarbon in bag, parts per million by weight,

$P_{purge\ gas}$ = density of purge gas, g/ml.

The emission rate of volatile hydrocarbons can then be calculated with the following equation:

$$ER_{water} = \frac{500(f_w)(VO_i - VO_o)}{V_s}$$

where

ER_{water} = emission rate of hydrocarbon, lb/hr,

f_w = flow rate of water through system, gal/min,

VO_i = volatile organics in the inlet water stream, grams,

VO_o = volatile organics in the outlet water stream, grams,

V_s = volume of sample, ml.

5.4.3 Total Organic Carbon

Total organic carbon assays were accomplished with a Dohrmann DC52D TOC Analyzer. This instrument oxidizes organics to carbon dioxide and then reduces the carbon dioxide to methane. The methane is measured with a flame ionization detector.

The instrument is zeroed using a "zero carbon water standard" especially prepared for this analysis by Radian. The water is deionized, filtered and distilled from potassium permanganate under helium with a high reflux. This has proven to be superior to commercial standards. The standard for the analysis is 180 ppm carbon in water available from Dohrmann.

Several replications of each sample were required because the size of the portion of the sample actually analyzed is so small (30 μℓ) that it is difficult to obtain a representative portion.

6.0 SPECIES CHARACTERIZATION

6.1 Organic Species

The measurement of organic species was accomplished by a combination of experimental methods employing gas chromatography and mass spectrometry (GC/MS), as described in the following subsections.

Samples were collected and analyzed for characterization of the following:

- point source emissions such as CO boiler regenerator flue gas,
- fugitive emissions from valves, pumps, etc., and
- effluent streams from wastewater treatment processes.

6.1.1 Qualitative Analysis

6.1.1.1 Instrumentation

Analyses for organic species were performed in Radian's GC/MS laboratory. The instrumentation used is summarized in Table A6-1.

TABLE A6-1. MASS SPECTROMETERS - RADIAN

Instrument	No.	Type	Maximum Resolution	Ionization Modes	Sample Inlets	GC/MS Interface	SIM[1]	Data System	Other Features
Hewlett-Packard (5982)	1	**Quadrapole**	Unit	EI,[2] CI[3]	GC, Probe	Glass jet or membrane or direct	Yes	Hewlett-Packard (5933)	Capillary GC, Subambient GC, Purge and Trap VOA Analysis
Hewlett-Packard (5985)	1	**Quadrapole**	Unit	EI,[2] CI[3]	GC, Probe	Glass jet or direct	Yes	Hewlett-Packard (ZIMX-E)	Capillary GC, Subambient GC, Purge and Trap VOA Analysis
	1							Hewlett-Packard (5934 A)	Disc - Tape Interface digital tape unit, zeta plotter, acoustical telephone coupler

[1] SIM = Selected Ion Monitoring.

[2] EI = Electron Ionization.

[3] CI = Chemical Ionization.

6.1.1.2 Extraction

Depending on the sample type and emission source, different analytical procedures were employed to adequately measure the organic species. Table A6-2 lists the sample type received and the analytical procedures employed for each sample. Each of these procedures will be described in the following subsections.

Preliminary Sample Treatment--The analysis of trace organic species by GC/MS required preliminary sample treatment. These preliminary steps and their purposes were:

- isolation, to remove the organic species or interest,
- separation, to divide the isolated organic species into groups of similar chemical or physical properties,
- enrinchment, to increase the concentration of the organic species.

Each of the samples collected during this work required some or all of these steps as described below.

Isolation of the Organic Species--Removal of the organic species was performed by two techniques, solvent extraction and thermal desorption. The thermal desorption of volatile species from Tenax tubes is an integral part of the analysis and, as such, will be discussed later.

TABLE A6-2. SUMMARY OF SAMPLE TYPES AND ANALYSIS PROCEDURES

Sample Type	Sample Composition	Emission Source	Analytical Procedure
Process Liquid	Organic Liquid	Fugitive	Pentane Dilution[1]
XAD-8 Resin	Sorbed organic vapor	Fugitive	Pentane Dilution[1]
Tenax	Sorbed organic vapor	Fugitive	Thermal Desorption
XAD-2 Resin	Sorbed organic vapor	Point	ABN
Particulate	Particulate	Point	ABN
Effluent Water	Aqueous	Point	Ether extraction
Charcoal	Sorbed organic vapor	Fugitive	CS_2 extraction

[1] Some samples also fractionated on silica gel.

The determination of trace organic species requires special precautions in the sample preparation. Only high-purity distilled-in-glass solvents were employed. All laboratory glassware was cleaned with chromic acid before use. Immediately prior to use, the glassware was rinsed with an organic solvent to remove any traces of organic material. Only Teflon, glass or stainless steel labware contacted the sample. Aqueous reagents were presaturated with solvent before use.

Isolation of the organic species from the XAD-2 resin and particulate samples was performed by a 24-hour Soxhlet extraction with diethyl ether. Diethyl ether was preferred because:

- it has been demonstrated that ether is a superior solvent for removal of polynuclear aromatics and other species from XAD-2 resin, and
- any water associated with the resin is removed by the ether.

The XAD-8 resin samples were Soxhlet extracted with pentane. A minimum quantity of solvent was employed for the extraction in order to minimize the loss of volatiles through concentration. Pentane was also employed as the solvent for the process liquids. Typically, 1 to 2 grams of sample were dissolved in 100 ml of pentane.

Aqueous samples were manually extracted with diethyl ether in a separatory funnel.

Thus, at the conclusion of this phase of analysis, the organic species in each sample had been transferred to a different matrix as summarixed in Table A6-3. The process liquid and XAD-8 sample extracts were ready for analysis. The effluent water sample still required concentration as described later. The XAD-2 resin and particulate sample extracts were further separated as described in the following section.

The ABN Separation/Derivitization Scheme--The acid-base-neutral (ABN) separation strategy was developed by Radian Corporation for the analysis of complex environmental samples. The ABN approach is illustrated schematically in Figure A6-1. The strategy is based on a series of liquid-liquid extractions that separate a sample into three principal fractions:

A - organic acids whose salts partition into water at high pH,

B - organic bases whose salts partition into water at low pH, and

N - neutral hydrophobic compounds.

These principal fractions are then further subdivided to yield a total of seven fractions which are analyzed by GC/MS.

The ABN extraction procedure was employed to characterize the semi-volatile organic species in the XAD-2 resin and particulate samples. This separation scheme was chosen on the basis that (1) the distribution of compounds throughout the procedure can be predicted with reasonable accuracy, (2) the procedures do not involve elevated temperatures and (3) the number of fractions presented for analysis is minimal.

TABLE A6-3. SUMMARY OF ISOLATION PROCEDURES

SAMPLE TYPE	ORIGINAL MATRIX	NEW MATRIX	ADDITIONAL SAMPLE TREATMENT
Process Liquid	Organic Liquid	Pentane Solution	None
XAD-8 Resin	Polymeric Absorbant	Pentane Extract	None
Tenax	Polymeric Absorbant	Polymeric Sorbant (unchanged)	None
XAD-2 Resin	Polymeric Absorbant	Ether extract	ABN
Particulate	Particulate	Ether extract	ABN
Effluent Water	Aqueous	Ether extract	Concentration

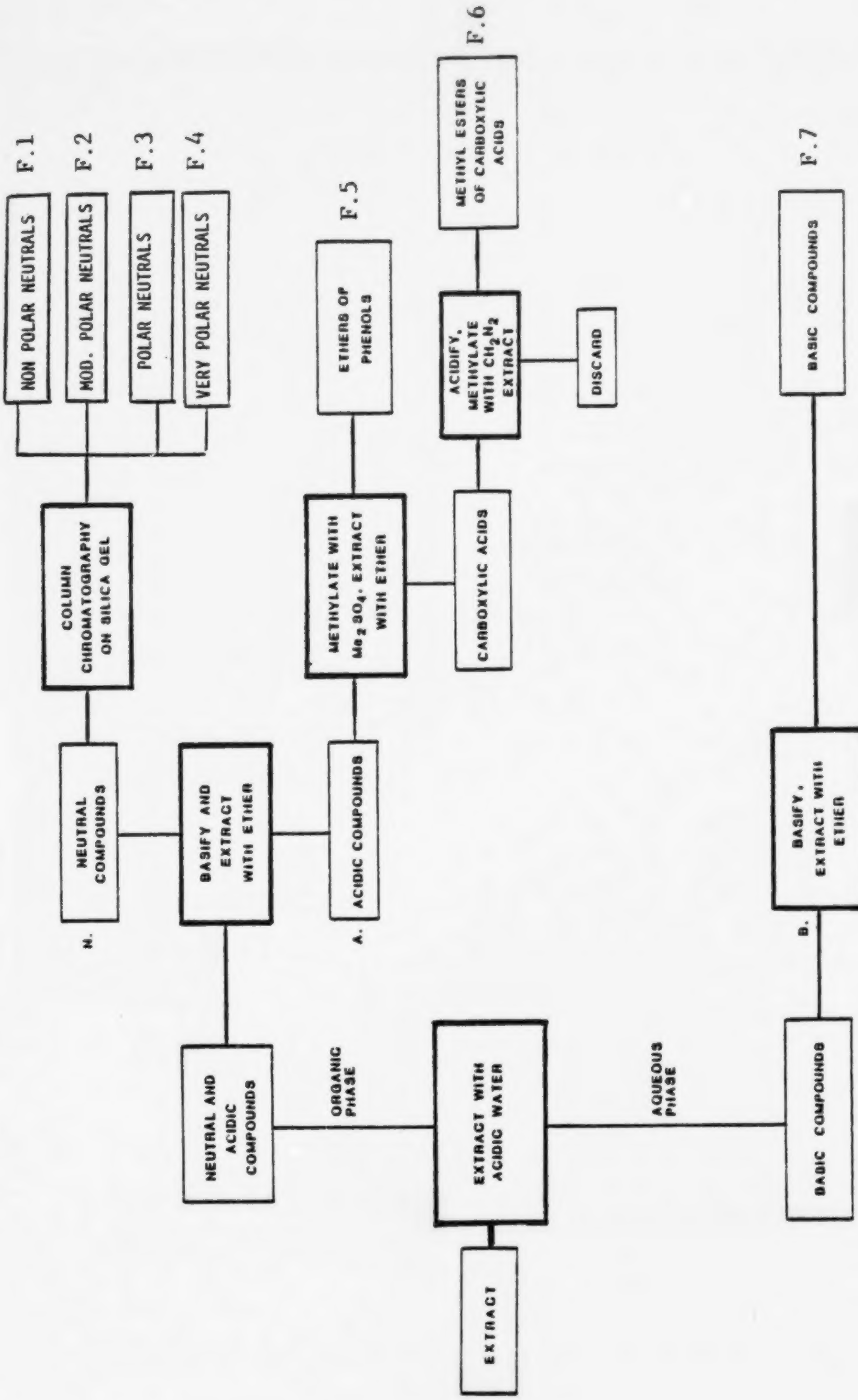

EXTRACT
EXTRACT WITH ACIDIC WATER
ORGANIC PHASE
AQUEOUS PHASE
NEUTRAL AND ACIDIC COMPOUNDS
BASIC COMPOUNDS
BASIFY AND EXTRACT WITH ETHER
N.
NEUTRAL COMPOUNDS
A.
ACIDIC COMPOUNDS
COLUMN CHROMATOGRAPHY ON SILICA GEL
NON POLAR NEUTRALS
F.1
MOD. POLAR NEUTRALS
F.2
POLAR NEUTRALS
F.3
VERY POLAR NEUTRALS
F.4
METHYLATE WITH Me2SO4. EXTRACT WITH ETHER
ETHERS OF PHENOLS
F.5
CARBOXYLIC ACIDS
ACIDIFY, METHYLATE WITH CH2N2 EXTRACT
DISCARD
METHYL ESTERS OF CARBOXYLIC ACIDS
F.6
B.
BASIFY, EXTRACT WITH ETHER
DISCARD
BASIC COMPOUNDS
F.7

Figure A6-1. ABN Scheme

The purpose of the separation scheme was to effect a sufficient division of organic components so that those compounds of primary interest could be identified and quantitated. This scheme was not intended to be the ultimate in separations, and it was not intended that every compound collected in a particular sample would be isolated and identified.

The complete ABN separation scheme is described in the subsections below.

Separation of Neutral, Acidic, and Basic Species--The ether extract of the XAD-2 resin, in particular, was extracted with three 100 ml portions of five percent HCl in a separatory funnel. The combined acidic and neutral extract was then separated as described later. The pH of the aqueous phase was adjusted to a pH of 11 with NaOH pellets and then extracted with three 100 ml portions of ether. This ether extract containing basic species was then concentrated.

The acidic/neutral extract was extracted with three 100 ml portions of five percent NaOH. The remaining neutral extract was separated while the basic aqueous extract was extracted and derivatized.

Separation of Neutral Compounds--The ether extract containing the neutral species was dried by passing it through a column of sodium sulfate and then concentrated to 1 ml. Hexane (10 ml) was then added and the sample was reconcentrated to 5 ml to remove the ether.

Silica gel (E Merck, grade 60, 70 - 230 mesh) was fully activated by placing it in an oven at 180°C for four hours. A small plug of glass wool was placed in the tip of a

1 cm × 100 cm column and the silica gel was transferred while still hot to a depth of 70 cm. A 1 cm bed of sand was placed on top of the packed silica gel and 100 ml of dry n-hexane was added to the column. The hexane was eluted using enough nitrogen pressure to give a flow rate of about 5 ml per minute. The flow was stopped when the solvent level reached the top of the bed and the quantity of hexane eluted was measured. The void volume of the column was calculated according to the following equation:

$$V = (\text{ml hexane added}) - (\text{ml hexane measured})$$

The hexane concentrate containing the neutral compounds was then transferred to the silica gel column and the receiver was rinsed with a small volume of hexane which was added to the column. The reservoir was filled with hexane. As the solvent level dropped, a total of 5 column volumes was added. When the solvent reaches the bed, five column volumes of the next solvent are added after the receiver is rinsed with small portions of this solvent. In a similar manner, five column volumes of each succeeding solvent combinations were added to give a total of four fractions.

The solvents and desired order were:

- F-1, Nonpolar neutrals, eluted with hexane,
- F-2, Moderately polar neutrals, eluted with 1:1 hexane: methylene chloride,
- F-3, Polar neutrals, eluted with 99:1 methylene chloride: methanol, and

- F-4, Very polar neutrals, eluted with methanol.

Each fraction was collected and then concentrated.

Separation and Derivatization of Acidic Compound--The alkaline extract containing the acidic compounds was methylated in two steps to convert phenols into methyl ethers using dimethyl sulfate and carboxylic acids into methyl esters using diazomethane to yield fractions F-5 and F-6 as described below.

The alkaline extract was placed in a 250 ml round bottom flask and 10 ml of 60 percent NaOH was added. The flask was heated to 90°C after which time 10 ml of dimethyl sulfate was added dropwise over a period of ten minutes. After the addition of dimethyl sulfate, the mixture was stirred for one hour. After the excess dimethyl sulfate was destroyed by addition of 5 ml of 50 percent NaOH, the mixture was cooled to room temperature. The aqueous mixture was then extracted in a continuous extractor for 24 hours with ethyl ether. The ether extract containing the ethers of phenols was concentrated to 1 ml.

After extracting the phenol ethers, the alkaline solution was acidified with 6N HCl to a $\mathrm{pH} \leq 2$. This acidic solution was extracted in a continuous extractor for 24 hours with ethyl ether. The ethereal extract was concentrated to about 1 to 2 ml and then transferred to an open hypo-vial. About 1 ml of a diazomethane solution prepared as described below was added to the extract concentrate. After swirling the mixture, more diazomethane was added until a yellow color persisted. The mixture was allowed to sit for 15 minutes with occasional swirling. The excess diazomethane was then removed by evaporation on top of a steam bath. The solution containing methyl esters of carboxylic acids was concentrated.

Diazomethane was prepared in a special distillation apparatus that has Clear-Seal joints in place of ground glass joints to prevent possible explosions (Adrich cat. #210-0250). The preparative procedure which follows was supplied with this kit. Twenty-five ml of 95 percent ethanol is added to a solution of KOH in water (5g in 8 ml) contained in a 100 ml distilling flask fitted with a dropping funnel and a condenser. The condenser is connected to two receiving flasks in series, the second containing 20 to 30 ml of ethyl ether. Both receivers are cooled to 0°C.

The flask containing the KOH solution is heated in a water bath to 65°C and a solution of 21.5g (0.1 mole) of Diazald in about 200 ml of ethyl ether is added through the dropping funnel in about 25 minutes. When the dropping funnel is empty, another 40 ml of ether is added and the distillation is continued until the distilling ether is colorless. This distillate contains about three grams of diazomethane.

Concentration of Sample Extract--Each of the sample extracts generated in this separation scheme were concentrated before analysis. Radian employed both macro and micro Kuderna-Danish (K-D) concentrators for this purpose. Typically, an extract was concentrated to 5 - 10 ml in a large K-D and then further concentrated to 1 ml in a micro K-D. An internal standard, d_{10}-anthracene was then added to each extract at a known level, typically 200 ppm. All sample concentrates were stored in crimp-top vials with Teflon-lined seals.

6.1.1.3 Identification of Individual Components

Each extract generated as described previously was analyzed by combined gas chromatography/mass spectrometry (GC/MS) utilizing either a Hewlett-Packard Model 5982 or a Hewlett-Packard Model 5985 Computer system. Both capillary and packed column gas chromatography were employed as described in the following subsections.

Identification of the chromatographic peaks was achieved by analysis of the individual mass spectra. Interpretation of mass spectra was performed by three approaches:

- manual interpretation of an unknown mass spectrum,
- comparison of the unknown mass spectrum against the mass spectrum generated from the analysis of a previously analyzed standard, or
- computer search of the unknown mass spectrum against libraries containing reference spectra.

In addition, another technique was utilized to identify selected organic species at trace levels. This technique, termed selected ion current profile (SICP) searches, is based on the appearance of key ions within a narrow retention time window. This technique was utilized to search for certain compounds, especially polynuclear aromatic hydrocarbons, in the extracts. Figure A6-2 presents a SICP search for some polynuclear aromatics in the ABN Fraction 2 from an XAD resin

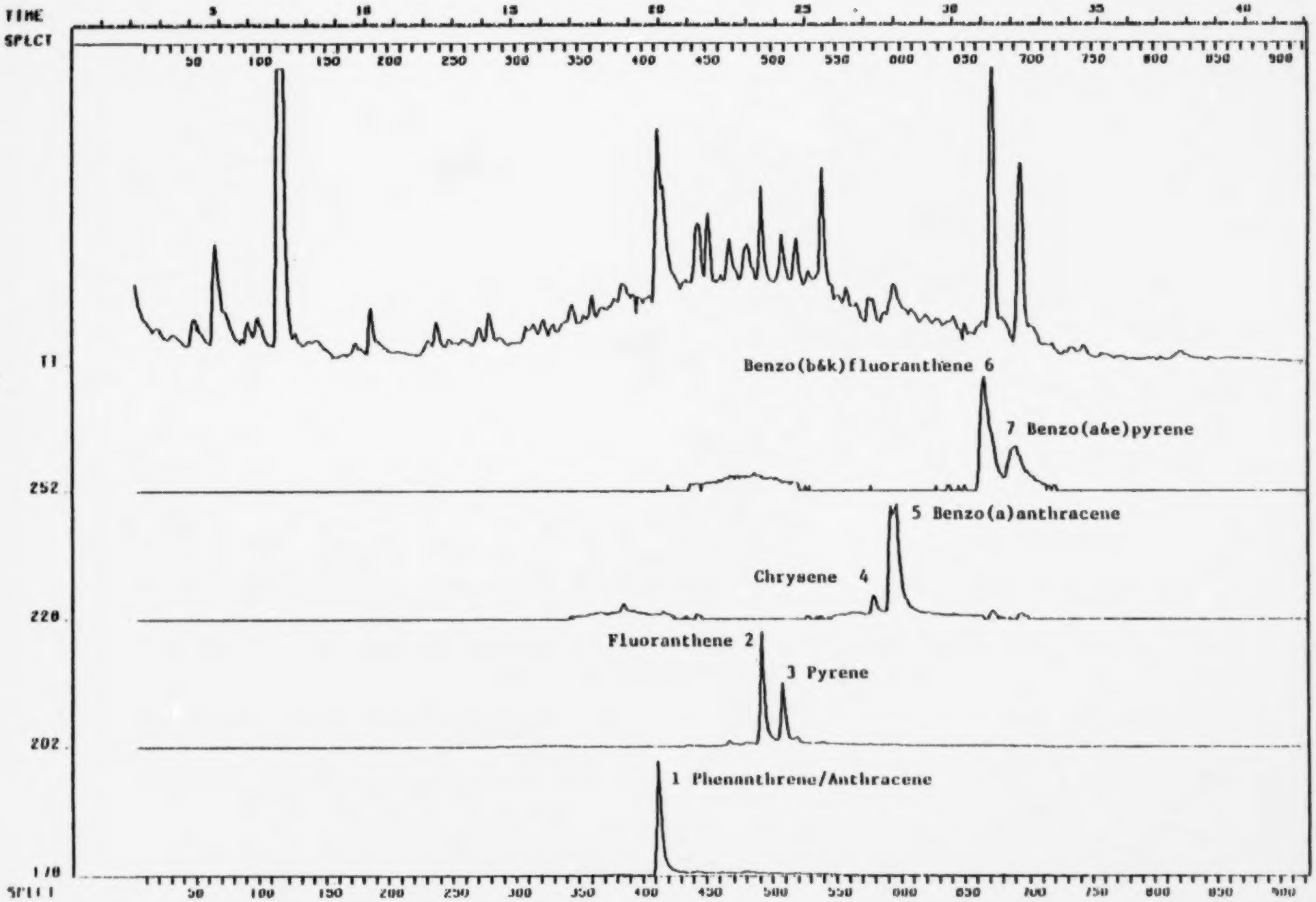


Figure A6-2. Total and Selected Ion Current Plots Obtained From The Analysis of An XAD-2 Sample Extract, Fraction 2

extract. Identification of the suspected compounds was confirmed by examination of their mass spectra.

Analysis of ABN Sample Extracts--Each extract from the ABN separation scheme was analyzed on a six-foot chromatographic column containing one percent SP-2250 on 80/100 Supelcoport. Typically, 2μℓ of each sample extract was injected onto the column.

The GC conditions were as follows: After an initial hold at 50°C for four minutes, the column was temperature programmed to 260°C at 8°C per minute. The organic species which eluted from the gas chromatograph were transferred to the ion source of the mass spectrometer by means of a glass jet separator. The mass spectrometer was scanned continuously from m/e 50 to m/e 350 with a cycle time of three seconds.

Analysis of Process Liquids and XAD-8 Extracts--The process liquid and XAD-8 extracts were analyzed by capillary GC/MS employing a special large bore 60 M SP-2100 WOOT capillary column. The chromatographic and mass spectrometer conditions were the same as the ABN analysis with 1μℓ of each sample injected.

Analysis of Tenax Tubes--Volatile species were determined by thermally desorbing the organics sorbed onto the Tenax tubes into the GC/MS system. A Tekmar Liquid Sample Concentrator was employed for this purpose. The sample was desorbed by rapidly heating the Tenax trap to 180°C and passing a helium flow over the sorbent. The sorbent tube effluent was connected directly to the head of a cold (- 40°C) gas chromatographic column. A 9-foot column packed with Carbopack C (80/100 mesh) coated with 0.2 percent Carbowax 1500, preceded by a one-foot section packed with Chromosorb W coated with three percent Carbowax 1500 was employed for this analysis. Quantitative analysis was achieved by injecting 50 ng of d_8-toluene in methanol onto the cold chromatographic column.

The mass spectrometer was operated in the repetitive scanning mode, scanning continuously from m/e 45 to m/e 300. Electron impact (70 eV) ionization was also employed for this work. After the thermal desorption was completed, the gas chromatograph was rapidly heated to 60°C. The temperature was held at 60°C for four minutes and then temperature programmed to 170°C at 4°C per minute. The temperature was held at 170°C until all of the volatile species had eluted.

6.1.2 Semi-Quantitative Analysis

Semi-quantitative analysis of the identified compounds was achieved by measurement of the area under the selected ion current profile for each compound. For a given compound, the area under the most abundant ion was calculated using the data system. The computed area was then compared against the area found from the most abundant ion of the appropriate internal standard, d_{10}-anthracene or d_8-toluene. The concentration of the species is then calculated using the following equation:

$$C = \frac{Ac \times Ca}{Aa \times R}$$

where C is the concentration of the component. Ac is the integrated area of the characteristic ion from the selected ion current profile, R is the response factor for this component relative to the internal standard, Aa is the integrated area of the characteristic ion for the internal standard and Ca is the concentration of the internal standard in the sample.

Radian determined response factors for many compounds relative to d_{10}-anthracene and d_8-toluene. Where the response factor was not known, a value of 1.0 was employed.

Electron impact (70 eV) ionization was employed exclusively for analyses. The mass spectral information obtained was stored on a magnetic disc for future interpretation and reference.

6.2 Inorganic Species

Inorganic analyses were performed by Commercial Testing and Engineering using spark source mass spectroscopy. Spark source mass spectrometer provides an extremely attractive tool for analysis of inorganic elements other than carbon, nitrogen, oxygen and hydrogen if great accuracy is not required. SSMS is not employed for the determination of mercury (due to high volatility loss). Detection limits for other elements are of the order of tens of parts per billion except for heavy elements such as lead, thorium, and uranium, for which the detection limits are somewhat higher. Mass spectra are recorded on ion-sensitive photoplates at a nominal resolution (m/ m) of 5000. Several different exposures of the same sample are recorded on a given photoplate and the concentration of the elements may be computed by visual interpretation. Isotope dilution studies can also be made to determine the concentration of a few elements with extremely high accuracy.

7.0 CONVERSION FACTORS

To Convert From	To	Multiple By
Btu	kcal	0.252
bbl	ℓ	159.0
gal	ℓ	3.785
ton	kg	907.2
lbs	kg	0.454
cm	in	0.394
ft^3	m^3	0.0283
psi	kg/cm^2	14.223
g/gal	g/ℓ	0.264
Btu/bbl	kcal/ℓ	0.0016
kWh/bbl	kWh/ℓ	0.0063
lb/bbl	kg/ℓ	0.0285
$lb/10^6$ Btu	g/Mcal	18.0
$grain/ft^3$	g/m^3	2.29
$gal/10\ ft^3$	$\ell/10^6m^3$	133.7
gpm	m^3/hr	0.227
lb/1000 gal	mg/ℓ	119.8

APPENDIX A: REFERENCES

1. Environmental Reporter. Federal Regulations, Vol. 2, 121:1559-1564.

2. Environmental Reporter. Federal Regulations, Vol. 2, 121:1569-1572.

3. Environmental Reporter. Federal Regulations, Vol. 2, 121:1567-1572.

4. Martinez, J. L. Summary of Analytical Procedures Used at the Mohave NO_x Pilot Unit, Austin, Texas, Radian Corporation (1975).

5. Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes, EPA 625-/6-74-003, Washington, D.C., Environmental Protection Agency, Office of Technology Transfer (1974).

6. Steigerwald, B. J. Emissions of Hydrocarbons to the Atmosphere from Seals on Pumps and Compressors. Report No. 6. Joint District, Federal and State (California) for the Evaluation of Refinery Emissions (April 1958).

7. Code of Federal Regulations 40, Protection of the Environment, Parts 60-99, revised edition, Washington, D.C., General Services Administration, Office of the Federal Register (July 1976).

8. Hamersma, J. W., S. L. Reynolds, and R. F. Maddalone. IERL-RTP Procedures Manual: Level 1 Environmental Assessment. EPA-6007 2-76-160a, EPA Contract No. 58-02-1412. TRW Systems Group, Redondo Beach, California (June 1976).

9. Texas Air Control Board. Laboratory Methods for Determination of Air Pollutants, revised edition, Austin, Texas (June 1976).

10. National Institute for Occupational Safety and Health. NIOSH Manual of Analytical Methods, NIOSH Division of Laboratories and Criteria Development, HEW Publication No. (NIOSH) 75-121, Cincinnati (1974).

11. Gallant, R. F., J. W. King, P. L. Levins, and J. R. Piecewicz. Characterization of Sorbent Resins for Use in Environmental Sampling, EPA-600/7-78-054, March 1978, Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, N.C. 27711.

12. Lentzen, D. E., D. E. Wagoner, E.D. Estes, and W. F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA-600/7-78-201, October 1978, Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, N.C. 27711.